Vol. XXVII. [MAY, 1905.] No. 5.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.[1]

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Received March 13, 1905.

CONTENTS.

Introduction 459
Balance and weighing 465
Preparation of pure materials 467
Water 467
Hydrochloric acid 467
Sodium chloride 467
Silver 472
Lime 481
Utensils 481
The solubility of silver chloride 481
The occlusion of dissolved substances by silver chloride 487
The ratio of sodium chloride to silver chloride 492
The ratio of sodium chloride to silver 502
The fusion of sodium chloride in vacuum 513
The synthesis of silver chloride 515
The new atomic weights of sodium and chlorine and their effect on other atomic weights 525
Summary 528

THE investigation of the atomic weights of the extremely common elements, sodium and chlorine, was undertaken because of an

[1] Presented, in abstract at the Philadelphia meeting of the American Chemical Society. Reprinted from Publication 28, Carnegie Institution of Washington, D. C.

unaccountable discrepancy which appeared in the composition of a sample of very pure sodium bromide, as compared with the results of Stas. This sodium bromide had been prepared for the purpose of determining the transition temperature of its hydrated crystals; and a preparation which yielded a constant transition point, therefore giving evidence of great purity, nevertheless possessed a perceptibly lower combining weight than that indicated by Stas's results.

Such a discrepancy as this was not to be passed over lightly. It indicated either an unknown constant impurity in our sodium bromide—and hence a possible error in our transition temperature —or else a flaw in the classical work of Stas. When the first cause of disagreement had been carefully sought in vain, the second was pursued.

Thus a physico-chemical investigation demanding great purity of materials led to a quantitative research of unexpected magnitude; and in turn this quantitative investigation depended continually upon physico-chemical methods and considerations. In confirmation of previous work in this laboratory, it was found that the physico-chemical conditions of experiment were of as serious import as the purity of the materials, and of far greater significance than an increase in the scale of operations. The essential circumstances here defined must receive consideration in any other research of a similar kind.

It is needless to say that an investigation seeking to test the accuracy of Stas's work is a serious undertaking, for undoubtedly much of his work deserves a rank among the most accurate of quantitative chemical results; certainly he distanced all those who preceded him. Nevertheless, he was by no means infallible, as his long oversight of the solubility of silver chloride, his difficulty in obtaining colorless ammonium bromide, the uncertainty concerning the oxygen in his silver, and the recent proof of a serious error in his work on iodine,[1] all testify. Moreover, Stas's work is not to be considered as accurate in proportion to the scale of his experiments, as many have been inclined to suppose. Mere increase in quantity of material can avail nothing if the same physico-chemical error or the same chemical impurity contaminates the whole. Indeed, it is doubtful if beyond a moderate scale of

[1] The work of Ladenburg and Scott has been confirmed by Dr. G. P. Baxter, of Harvard University, whose recent analyses show that the atomic weight of iodine can hardly be lower than 126.97. *Proc. Am. Acad.*, **40**, 419 (1904). This Journal, **26**, 1577.

operations increase of quantity decreases even the probability of accidental error. For example, the extreme variations in his work on the synthesis of silver chloride, in which on the average nearly 200 grams of the compound were weighed in each analysis, amounted to 0.006 per cent, or 12 milligrams of material.[1] An accuracy of 0.6 milligram with 10 grams of substance, very easy to attain as far as the collection and weighing of the material is concerned, would have brought him as good agreement. But large quantities have no advantage to offer, besides the increased accuracy in weighing and the diminished percentage effect of a given accidental loss of material in transference. For this reason the use of extremely large quantities must rather be considered as evidence of a lack of sound judgment than an index of unusal accuracy. Stas himself acknowledged this by using only about 10 grams of material in each of his last experiments[2].

Regretfully one must admit that a critical study of the work of Stas upon sodium in particular reveals several possibilities of error, as well as at least one inconsistency. He analyzed both the chloride and the bromide; of these salts the former received the greater attention, and will be discussed here in greater detail.

In reviewing his results upon sodium chloride there are two series to be considered, separated by an interval of time of over twenty years. Although at first sight these two series seem to have yielded almost identical results, as a matter of fact they are essentially inconsistent with one another. Both results were obtained by the method of Gay-Lussac, titrating weighed amounts of silver in solution with salt; but at the earlier time the latter was added until all precipitation ceased, while at the later time equivalence was assumed when the supernatant liquid gave equal opalescence with excess of either chloride or silver. Any one with experience will recognize that a much higher apparent atomic weight of sodium was to be calculated by the first procedure than by the second, other conditions being the same, and yet the results were almost identical. The immediate inference is, of course, that some other condition or conditions must have varied in order to compensate for the effect of the altered method of titration. This inconsistency, which appears also in his work on potassium and ammonium, has never been explained, and one of the functions of the present work was to account for it.

[1] J. S. Stas : Oeuvres Complètes (Brussels, 1894), 1, 341.

[2] *Ibid.*, 3, 503.

Among the possible sources of error in Stas's work, the most serious seems to have been the practice of dropping solid salt into the solution of silver nitrate.[1] Of course this practice caused the greater part of the silver chloride to be precipitated in the presence of a concentrated solution of salt, immediately around the solid—a circumstance tending greatly to promote the occlusion or inclusion of sodium chloride in the precipitate. Stas, in his early work especially, was fully awake to the danger of the occlusion of *silver nitrate* in this precipitate;[2] but he seems to have had no fear of occlusion of other salts. In the sequel we shall show that the chloride of silver tends to carry down with it many salts from their concentrated solution, and that the details of treatment determine whether or not these impurities may be removed by washing.

Another possible cause of the discrepancy is to be found in the methods used for preparing the materials. In Stas's earlier investigation, where the analytical end-point was erroneous, greater care was taken in preparing the sodium chloride than in the later experiments. In general, when purifying this salt, he employed violent treatment, and very rarely recrystallized or in any way fractioned his material afterwards. His favorite method was fusion with ammonium chloride and ammonium chlorplatinate. Presumably the ammonium chloride was used to expel other halogens, and the deposited platinum, Stas believed, carried down silica and alumina with it. Except for these possible advantages, this admixture of foreign materials seems to be a doubtful expedient. In the ten experiments of 1860,[3] six different preparations were made, from the following sources:

(1) Sodium carbonate neutralized with hydrochloric acid.

(2) Rock salt recrystallized.

(3) Sodium sulphate repeatedly fused with ammonium chloride.

(4) Sodium tartrate recrystallized and fused with ammonium chloride.

(5) Sodium nitrate, similarly treated.

(6) Sodium chlorplatinate recrystallized and fused.

The final step in every case consisted, as usual, in mixing the salt with ammonium chloride and ammonium chlorplatinate, fusing until colorless, and decanting the fused mass from the residue. The ten

[1] Oeuvres, **1**, 759; also II, 479.

[2] *Ibid.*, **1**, 337.

[3] *Ibid.*, **1**, 365.

results agreed almost exactly, indicating that the preparations were, at least, identical; but, of course, the results are all in error, because of the erroneous end-point.

Only two preparations were used in the four experiments of 1881.[1] For one of these, impure sodium bicarbonate was neutralized with hydrochloric acid. The salt, after three recrystallizations, was repeatedly fused with ammonium chloride and chlorplatinate[2]. By evaporating a solution of the resulting salt with chlorplatinic acid, it was converted into sodium chlorplatinate without fractionation of any kind. About nine-tenths of this material was dissolved in water. Stas assumed that any potassium salt would not then dissolve; but this possibility is by no means excluded. The first lot of crystals from the solution was decomposed and fused, and the resulting sodium chloride used in the first two experiments. A second and third lot were also obtained from the mother-liquor of the first lot. The salt made from the third lot was employed in the fourth experiment of 1881. Thus there were only four crystallizations between the starting-point (which was admittedly impure) and the final product; and the first three of these crystallizations were of common salt, isomorphous with potassium chloride. In the third experiment of 1881, the salt was made by neutralizing pure acid sodium carbonate and repeatedly fusing with ammonium chloride in platinum with no fractionation at all. These specimens were probably less pure than the earlier ones.

Thus it appears that every preparation of Stas was fused in contact with platinum, which was usually in a finely divided "nascent" condition, or at least in the presence of decomposing ammonium chloride. The question is therefore important whether or not platinum can dissolve in melted salt at the temperature of 800°. We have found that fused salt when pure has but a very slight dissolving effect upon platinum, but in the presence of ammonium chloride or hydrochloric acid at a red heat in the presence of air a noticeable quantity of platinum is dissolved, as is indicated by the loss of weight of the containing crucible. It seems likely, then that Stas's material contained traces of platinum; either in a very finely divided state or possibly as a salt platinum; but the amount could hardly have been large. Stas invariably found non-volatile residues in his preparations, consisting of silicates of

[1] Oeuvres, I, 755.
[2] *Ibid.*, p. 685.

sodium and calcium, which he discovered by vaporizing the salt. These residues usually amounted to about 0.004 per cent. It is not impossible, however, that yet other impurities might have volatilized with the sodium chloride. In volatilizing his salts Stas used a boat of *pure platinum*.[1] It is possible that pure platinum would itself have volatilized appreciably at the temperature required to drive off 10 grams of salt in half an hour.[2] For either of the two reasons just given, Stas's correction for impurity in his salt would not have been large enough.

These impurities must, however, have been almost equally present in the early and later samples, and could not explain the serious discrepancy between them. At most, however, as we shall show, they could hardly have exceeded 0.01 per cent. an amount much smaller than the discrepancy in question. Our own experience shows that common salt is a substance very easy to prepare in a pure state. Clearly the cause of the discrepancy must be sought elsewhere.

The other essential substance, to be prepared in a pure state, was silver. This Stas prepared in a variety of ways, as is well known; but for all this work the silver was either cast in ingots from under an oxidizing flux, or else "granulated" by dropping into water. His criterion of pure silver was the melting of the surface of a button without any apparent irregular expansion as it liquefied, or any flame color, and the absence of all specks and spots from the completely melted globule. In all experiments it was reddened in a silver crucible before weighing.

After Dumas had recommended the fusion of silver in a vacuum, Stas made many experiments upon the occlusion of gases by silver. He carefully investigated the samples of silver used in his atomic weight researches, and also new preparations. He found that fusion in a flux of sodium nitrate introduced a quantity of oxygen, and that bars and blocks were slightly purer than "granulated" silver. In no case was the amount of retained gas found by Stas enough to affect seriously even a very accurate analysis; but, as will be shown later, it is probable that he did not find all the oxygen present. An error in Stas's silver would not account for the discrepancy between his results on sodium and ours, for an impurity in the silver would cause his atomic weight of sodium to

[1] Oeuvres, **1**, 681.

[2] See Hall: This Journal, **22**, 494 (1900); Richards and Archibald: *Proc. Am. Acad.*, **38**, 460 (1903); Hulett and Berger: This Journal, **26**, 1512 (1904). There seems to be no doubt that platinum is slightly volatile at 1,000° in the presence of air. Probably it is not in pure nitrogen.

appear too low, and not too high. On the other hand, the impurity in Stas's silver is undoubtedly the cause of the difference between his atomic weight of chlorine and ours.

From these considerations it was clear that the reason for the incompatibility of the results on sodium was probably to be sought chiefly in the method of analysis, rather than in the impurity of the materials. The long-continued search for the causes of discrepancy led finally to a satisfactory explanation of the whole anomaly. In order to make this clear, the details of our own investigation must be recounted.

Balance and Weighing.

The Troemner balance which has served in many similar researches was used during most of the present work.[1] Successive weighings on it of the same object rarely differed as much as 0.03 milligram. For a few of the conclusive final experiments a yet more sensitive and perfect balance, especially made for this kind of work by the same maker, was used.

The Sartorius weights were standardized from time to time by the method devised by one of us.[2] It was found as usual that the larger gold-plated and platinum-plated brass weights changed very slightly from time to time, although the smaller platinum weights did not. All weighings were made by substitution. Furthermore the major portion of the substituted tare consisted of a counterpoise exactly similar to the crucible, tube or boat which was being weighed. Thus the weights required were never large in amount and errors due to changes in meteorological conditions were avoided. The method of recording and checking the weights is given in another place.[3]

While these obvious particulars are given here for the sake of completeness, it must be remembered that accuracy of weighing is easily attained. The great errors in chemical quantitative work are usually not in the weighing, but are due rather to impurities in the substances weighed or incompleteness or irregularity of reaction. Only in a few cases, with large vessels, was it necessary to use the telescope for reading the vibrations, the observer being in another room and looking through an intervening glass door.

The balance-room devoted to these most accurate determina-

[1] *Proc. Am. Acad.*, **26**, 242 (1891).
[2] Richards: This Journal, **22**, 144 (1900).
[3] Richards: *Proc. Am. Acad.*, **31**, 175 (1895); *Ztschr. anorg. Chem.*, **10**, 19 (1895).

tions was kept at a very constant temperature, being wholly inside a private laboratory whose air temperature was regulated by a delicate thermostatic attachment to its heating apparatus. The balance-room itself had neither heating apparatus nor outside windows. This question of constancy of temperature is of the most vital importance in the weighing of large vessels.

In reducing weights in air to weights in vacuum, the densities at about 20° were assumed to be as given below. The value for silver proceeds from Stas, and was checked by one determination by us of the purest silver (sample W, described later). The value for the brass weights refers to the gold-plated Sartorius weights used in all but a few of the experiments; the other set had a slightly higher density, of which account was taken. The correction for 1 gram of substance weighed in dry air at 20° and 760 mm. pressure is stated for each substance.

Substance.	Density at 20°.	Correction for one gram of substance, 20°, 760 mm.
Silver	10.49	—0.000029
Sodium chloride	2.14	+0.000418
Silver chloride	5.56[1]	+0.000073
Weights	8.40	.....

Especially when sodium chloride or silver chloride was weighed the temperature and barometric pressure were recorded at the time of weighing. In case of significant variations of temperature or pressure the corrections were changed accordingly. The correction is computed as follows:

Correction $= w$ (volume of 1 gram substance—volume 1 gram of weights), where w is the weight of 1 cc. of air at the given temperature and pressure. The following small table contains a sufficiently accurate statement of this value in convenient form for use with a logarithmic slide rule.

VALUE OF w IN GRAMS.

Temperature °C.	750 mm.	760 mm.	770 mm.
14	0.001214	0.001230	0.001246
16	0.001205	0.001221	0.001237
18	0.001197	0.001113	0.001229
20	0.001189	0.001204	0.001220
22	0.001181	0.001196	0.001212
24	0.001173	0.001188	0.001204

If the air is completely saturated with water vapor, the above values should be decreased by 0.000008 at 14°, 0.000010

[1] Richards and Stull, in an investigation as yet unpublished.

at 20°, and 0.000013 at 24°. But since the air of our balance cases was certainly less than a quarter saturated with moisture, correction on this account would have been supererogatory.

Preparation of Pure Materials.

Water.—The traces of organic impurity in the distilled water of the laboratory were eliminated by redistilling from a weakly alkaline solution of potassium permanganate, using at first a glass condenser and rejecting the first quarter of the distillate. Water thus prepared was pure enough for preliminary nephelometric work, when the presence of a trace of alkali could do no harm; it was usually kept in Jena flasks. In cases where the greatest purity was desired it was distilled, of course, once further, and for the nephelometric experiments it was kept in a closed bottle provided with a siphon and protected from possible traces of hydrochloric acid by a tube containing sodium hydroxide. For final preparations and accurate analyses, where silica and alkali must be excluded, the water was condensed and collected during the third distillation wholly in platinum. Care was taken to exclude dust in all stages of the proceedings; for, although visible dust might weigh little, its presence in a silver halogen salt would produce decomposition and loss of weight in the final fusion. Only one who has attempted to exclude all dust from solutions can appreciate the difficulty of doing so.

Hydrochloric Acid.—For the final work the purest acid of commerce was treated with a few crystals of potassium permanganate, diluted and boiled. This should have expelled bromine and iodine, and must have oxidized any trace of organic matter which might have been present. The oxidation and boiling were repeated. After the succeeding distillation the middle fraction was selected and subjected to a second distillation, in which a platinum condenser and receiver were employed. As a matter of fact, most of these precautions were found to be unnecessary, since salt made, as described below, from the best "chemically pure" acid of commerce only once redistilled in platinum, without any further precautions, gave the same results as the purest material.

Sodium Chloride.—In most cases a perfectly pure salt can not be made by precipitating the impurities, as many are prone to assume, but must itself be precipitated or crystallized from the

less pure solution. Sodium chloride is nearly insoluble in a concentrated solution of hydrochloric acid; therefore, the usual method of precipitation by means of hydrochloric acid gas, seemed the best possible method of obtaining pure sodium chloride, since any included hydrochloric acid could be completely expelled by fusion. This expectation was confirmed by trial, and when it had been found that this means of purification was unusually suitable, most of the specimens of salt were treated in this way. This and other purifications were greatly assisted by centrifugal draining of the crystals. For this purpose salt was collected in a platinum funnel, and this was covered and supported on a stout frame capable of being whirled by means of strong cord about a radius of a meter. A test-tube, firmly fixed in the frame, collected the separated mother-liquor. Centrifugal draining, so important in technical work, has hardly received the attention which it deserves in the scientific laboratory. Experiments have shown that a good centrifugal apparatus is capable of separating nine-tenths or more, according to the habit of the crystals, of the mother-liquor which would otherwise contaminate the solid, hence making the purification at least ten times as effective as it would otherwise be.[1] The whole treatment of precipitation and draining was carried on in platinum vessels which had been effectively freed from superficial iron.

Besides this chief mode of purification, others were used in special cases, and the original material came from a variety of sources, as recorded below. One of these was Merck's purest sodium chloride, which this firm stated had been prepared from German rock salt. Another was the very pure sodium sulphate prepared for the experiments on the transition temperature of this substance, and known to be very pure, because of the constancy and accuracy of its transition point (32.383°).[2] Another was a fine specimen of Stassfurt halite, perfectly clear and colorless. A fourth specimen was made from the purest sodium bicarbonate manufactured by the Solvay Process Company, of Syracuse, New York, and very kindly furnished in large quantity by that company. It is a pleasure to express our thanks for this courtesy. A fifth sample was made from pure sodium carbonate from Merck. These preparations, differing widely in the

[1] Richards: This Journal, **27**, 104 (1905).

[2] Richards and Wells: *Proc. Am. Acad.*, **38**, 431 (1902); also *Ztschr. phys. Chem.* **43**, 465 (1905).

steps of manufacture and in geographical source, all yielded essentially the same atomic weight.

The source of the materials having been given above, it remains to record the details of their preparation.

In the first place a large quantity of Merck's sodium chloride, which had been purified from German rock salt, was thrice reprecipitated by hydrochloric acid. This salt is designated "Sample A" below, and was used in preliminary experiments. It was further crystallized from water (B); some of this was fused with ammonium chloride and ammonium chlorplatinate (C); a portion was then precipitated with hydrochloric acid (D); and finally some was again fractionated from water (E). None of these operations seemed to have any essential effect upon the combining weight of the salt; hence, even "Sample A" must have been practically pure.

The very pure sodium sulphate was easily converted into chloride by successive precipitation from solution by means of gaseous hydrochloric acid. The sulphate forms an especially fortunate source of pure sodium, since none of the other alkaline sulphates yield crystals of the same degree of hydration or the same crystal form. Hence sodium sulphate which has been many times recrystallized must be extremely pure. The ease with which a constant transition temperature may be obtained is evidence of this.

A specimen of sodium sulphate, which had been shown to be pure by its transition temperature, was twice further recrystallized before adding hydrochloric acid. Four precipitations by this gas, with washings and drainings, removed practically all of the sulphuric acid. Nevertheless, when the mother-liquor was concentrated by evaporation and tested, an extremely small trace of sulphate was found by excess of barium salt to persist until the tenth precipitation. There was no trace of visible barium sulphate on testing the mother-liquor, even in the nephelometer, after the eleventh precipitation, but the salt was precipitated once more for certainty. This salt, thus twelve times separated by hydrochloric acid, was designated F. It seems highly probable that since so large an amount of sulphuric acid was eliminated from it by this treatment, all other impurities must have been separated.

For another specimen of salt a number of fine, large, colorless

transparent crystals of halite, from near Stassfurt, Germany, were dissolved in pure water. After the addition of a little sodium hydroxide, boiling and standing, the solution was filtered and precipitated with hydrochloric acid gas. A solution of the latter salt in water stood several days. The clear decanted portion was precipitated twice more, fractionally crystallized from water and dried over sodium hydroxide in a vacuum desiccator. This specimen was called sample G.

The bicarbonate from Syracuse, New York, was of the following composition, according to the report of the Solvay Process Company:

	Per cent.
Silica	0.006
Ferric oxide and alumina	0.002
Calcium carbonate	0.030
Magnesium carbonate	0.005
Sodium chloride	0.070
Sodium carbonate	0.522
Sodium bicarbonate	99.300

This material, already very pure for a commercial substance, was easily further purified by repeated washing with cold water, which was sufficient to remove most of the chloride.

A portion of the Syracuse bicarbonate, thus washed four times with cold water and thoroughly drained each time with a reverse platinum filter, was nearly all dissolved in water. After settling, the resulting clear solution was decanted, neutralized with hydrochloric acid and evaporated to dryness. The sodium chloride was fused in platinum, dissolved, and considerably diluted. After long standing the clear upper portion was decanted from very finely divided silica. This method of fusion is a very effective means of separating silica, but the precipitate is so fine as to require a long time to settle, and as to run through most filtering septa. Hence cautious decanting, with rejection of the considerable lower portion of the solution is necessary. The unimpeachable solution of salt thus obtained was concentrated and twice precipitated by hydrochloric acid gas (H), twice more precipitated (I), and yet twice more precipitated (J). Analysis showed these three to be alike, as will be recorded.

The Merck bicarbonate was thoroughly washed and once recrystallized from water. It was then gently ignited, and the normal carbonate was three times crystallized from water. From

this carbonate, by the usual process of precipitation by hydrochloric acid gas and crystallization from water, sample K was prepared. This sample gave essentially the same combining number as the others.

With such conclusive evidence that no foreign base was present, we turned our attention to the acid. The preceding preparations had all been precipitated with hydrochloric acid gas, obtained simply by warming the highly concentrated purest acid of commerce, because we deemed it more convenient to use this constant material, even if slightly impure, than to prepare so large a quantity of the purest acid. A special set of comparative experiments, made with the purest acid, proved that the other material had, as a matter of fact, been pure enough for the most exacting requirements.

For this purpose the very pure hydrochloric acid was used, whose preparation is described above (p. 467). This acid was neutralized by an especially prepared sample of soda, made from a second portion of the Syracuse bicarbonate. The elaborate purification took place wholly in platinum vessels, of course. After being washed as before, the bicarbonate was dried and heated, to convert it into the normal carbonate. The solution of the latter in water was decanted daily as long as any precipitated residue (calcium carbonate) appeared visible. The sodium carbonate was then recrystallized four times, as the deka- or hepta-hydrate, and once as the anhydrous salt. A concentrated solution of the latter salt was then treated for a considerable time with carbon dioxide under a bell jar until the bicarbonate had formed. The carbon dioxide was made by gently heating sodium bicarbonate, and was well washed with pure water. The pure bicarbonate thus formed was washed with cold water, thoroughly drained, and dissolved in an excess of the pure hydrochloric acid. The resulting salt was twice fractionally recrystallized from water on the steam-bath; and the crystals were washed and drained each time in order to free it from any possible calcium or magnesium chlorides, which are not easily eliminated from carbonate. Since the atomic weight from this preparation (L) was identical with that from the preceding preparations, the previous salts, made by precipitation with hydrochloric acid gas, could have contained no other halogen than chlorine.

It appears from the identity of all these specimens that sodium

chloride is among the substances whose preparation in a pure state is an easy problem. It is further true that the expulsion of water from it upon fusion without loss of halogen is a very simple matter; moreover, since we succeeded in proving that salt fused in a vacuum possesses the same combining weight as that fused in air, the solid contains neither occluded oxygen nor nitrogen in weighable amounts. This matter is further discussed on page 513.

Considering these experiments, it is fairly safe to infer that all the various preparations of sodium chloride were quite free from significant quantities of any foreign substance.

Silver.—Recrystallized silver nitrate served as the starting-point for the first specimens, and already purified residues from the early experiments were again converted into pure silver for later use. Many samples were prepared from different sources.

The silver used in all the experiments on sodium chloride was at first purified by precipitation as chloride and then recovered by reduction of the chloride with invert sugar[1] and sodium hydroxide. While it is true that this process is not the best for the final treatment of the silver, the precipitation as chloride is an excellent step in the preliminary purification. The invert sugar was made from a filtered solution of "rock sugar." No metals were found in it by electrolytic treatment. The sodium hydroxide used, after settling and decantation, had been electrolyzed until iron was completely removed. This slow but effective way of removing foreign metals was hastened by using a rotating cathode, while a fixed anode stirred the solution. The silver chloride was precipitated from a somewhat dilute solution, to avoid the occlusion of impurities, and must be thoroughly washed. It is best to wash at first with cold water, in order to avoid the contraction of the precipitate. The reduction was carried out in a silver dish to avoid the introduction of silicates. This precaution is not needed when electrolytic purification is to follow. In some cases, where the original material was not wholly free from suspicion, the precipitation as chloride and reduction were repeated. After reduction, the washed silver was fused upon either sugar charcoal or pure lime, before the blast-lamp, whose nozzle was scrupulously cleaned. If the large buttons

[1] According to Stas, saccharose at 100° would have answered as well as invert sugar at 60°. The saccharose is, of course, inverted by the strong hot alkali. Oeuvres, 3, 13.

of metal thus formed are not kept hot too long and are cooled in a reducing flame, they are already extremely pure.[1] For ordinary work, or even for work on atomic weights of usual accuracy, its purity suffices. Nevertheless, it can not be considered as perfectly pure, for it must contain, perhaps, 0.001 per cent. of sulphur and variable traces of carbon from the illuminating gas (or else oxygen from the air), as well as an occasional trace of silver chloride, arising from incomplete reduction. When thus cooled it is likely to contain numerous minute cells enclosing gas.

As one stage in the purification the electrolytic method used by J. L. Hoskyns Abrahall has many advantages.[2] The almost pure material just described is made the anode of a cell containing a concentrated solution of silver nitrate prepared from the same silver. The cathode is a pure silver wire, upon which is deposited by a properly regulated current beautiful crystals of electrolytic silver. The finely crystalline powder which falls from the anode[3] may be easily collected separately by placing the anode button in a watch-glass or low dish, wholly submerged in the electrolyte. In order to exclude every chance of contamination, no metal but silver may be allowed to come in contact with the electrolyte, although the danger from an immersed platinum wire, either at cathode or anode, is obviously slight. Three samples of silver were thus prepared, called respectively M, N and P. This silver must have been free from every conceivable impurity, except about 0.02 to 0.05 per cent. of the mother-liquor from which it was deposited.[4] This liquor, consisting wholly of water and silver nitrate, can be eliminated only by fusing the silver, a matter which will soon be discussed.

Besides this very pure material used in the work on sodium, several new samples of at least equal purity were made for the even more critical work on chlorine. Three of these new preparations were made from thrice crystallized pure silver nitrate. A portion of this nitrate was converted into silver chloride and reduced by pure invert sugar and purified sodium hydroxide. A second portion was reduced by the invert sugar and sodium hy-

[1] Richards: *Proc. Am. Acad.*, **29**, 65 (1893); *Ztschr. anorg. Chem.*, **6**, 98 (1893). See also *Proc. Am. Acad.*, **38**, 450 (1903). This work was confirmed in the latter part of the present investigation.

[2] *J. Chem. Soc.*, **61**, 660 (1892).

[3] Richards and Heimrod: *Proc. Am. Acad.*, **37**, 415 (1902).

[4] Richards and Heimrod: *Ibid.*, **37**, 415 (1902); Richards: *Proc. Am. Philos. Soc.*, **42**, 28 (1903); *Ztschr. phys Chem.*, **46**, 189 (1903); Stas, Oeuvres, **3**, 40.

droxide. A third portion was reduced by ammonium formate and ammonium acetate as recommended by Stas. Some of each of these lots was deposited by electrolysis in a concentrated silver nitrate bath in the usual way (S, T and U respectively).

Not content with these preparations—although all appeared to be equally pure—and anxious to leave no stone unturned whose lifting might disclose some new source of error, we made yet two more preparations with new precautions. For one of these, through the great kindness of Mr. Richard Pearce, of the Boston and Colorado Smelting Works at Argo, Colorado, a specimen of metal was secured whose source and history were known as far back as possible. Below is given Mr. Pearce's statement concerning it:

"This specimen is the product of the treatment of ores mainly from Colorado, in which it occurs associated with quartz, barite, calcite, pyrite, sphalerite, with more or less copper in the form of chalcopyrite, together with small quantities of arsenic, antimony, lead, bismuth and tellurium. The silver minerals are chiefly argentite, polybasite, pyrargyrite, proustite, tetrahedrite, stephanite, and occasionally cerargyrite. A small percentage of the silver comes in copper mattes purchased in other districts, more particularly Montana, where the silver ores are much the same in character, and are smelted with copper ores, forming a matte containing about 200 ounces of silver per ton.

"The roasted ore is mixed with others, principally siliceous, and the mixture is so arranged that, when smelted, it shall yield a slag containing as near as possible, 40 per cent. of silica and a first matte of fusible sulphide, which assays 40 per cent. of copper, 400 ounces of silver and 6 ounces of gold per ton.

"The first matte always contains a certain amount of lead, but the quantity rarely exceeds 10 per cent. The next stage in the process includes the roasting and concentration of the ore-metal, or first matte, to 'white metal' containing 60 per cent. of copper.

"This white metal is now ready for the extraction of the silver, which comprises the following operations: Rough roasting, fine grinding, fine roasting for sulphate of silver by Ziervogel's process, leaching and the precipitation of the silver on plates of copper.

"In the precipitation of the silver a certain amount of copper is found mixed with the silver in the form of cuprous oxide and of small scales and scraps of metallic copper, and a process of

refining is necessary previous to melting. This copper is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by means of a small jet of steam. Sulphate of copper is formed which is carefully washed out of the silver. The silver is then dried and melted into bars of an average fineness of 99.9 per cent.''

The silver came to us in the granulated form, obtained by dropping into water, and having been prepared with unusual care, was found to be even purer than Mr. Pearce claimed. After solution in nitric acid, it was crystallized *fifteen* times from acid solutions with centrifugal draining. The solubility in cold nitric acid is so slight, that this train of purification could be effected without serious loss. Even after the second crystallization, the salt was free from any observable trace of copper, and all other metallic impurities must have been eliminated before the last crystals were obtained. The pure silver nitrate was dissolved in pure water and precipitated by hot ammonium formate, prepared from pure freshly distilled formic acid and ammonia, which had been collected in platinum. It is better to use pure ammonium formate instead of a mixture of ammonium formate and acetate, as Stas did, because in the former case less carbon is included in the cells of the crystals, and moreover, that which is included, occurs in a less dangerous form. Because, the reaction takes place according to the following equation:—

$$2AgNO_3 + 2HCOONH_4 = Ag_2 + 2NH_4NO_3 + CO_2 + HCOOH$$

every 170 grams of silver nitrate need 46 grams of pure formic acid (or about 42 cc. of 90 per cent. acid (sp. gr. 1.2)) converted into ammonium formate. It is necessary to take this double amount in order that the ionized hydrogen (nitric acid) may be removed by the salt of the weaker acid. The precipitation was conducted in good glass. The beautifully white precipitate was washed with the purest water, until the washings gave no Nessler test. This silver, V,[1] although it had not been electrolyzed, was as pure as any which we made, judging from the analysis. The method of purification just described is the most convenient and safest of all. The only improvement, which might be suggested, is the use of a silver dish for conducting the precipitation. This improvement was tried in the next preparation.

[1] All the preparation work and analysis of this silver were conducted wholly by T. W. Richards.

Part of the silver, not electrolyzed, proceeding from the earlier reduction with ammonium formate and ammonium acetate was dissolved in redistilled nitric acid. The silver nitrate, once more crystallized, was dissolved in pure water in a large silver dish. Ammonium formate was freshly prepared by passing ammonia into redistilled formic acid. With it the silver was reduced in a silver dish, but otherwise as described above, washed free from ammonia, and dried in the same silver dish. This sample was called W.

There is no reason to believe that any of these samples of silver contained any appreciable impurity, except the traces of included mother-liquor, already alluded to. It is probable that Stas's silver, also, was equally pure at this stage in the proceedings. The subsequent treatment of the silver, in the effort to eliminate the mother-liquor and prepare the metal for weighing, seemed to be, in our experiments, the only cause of difference in the quantitative behavior of our samples, and there is every reason to believe that Stas introduced, during this treatment, the impurities which have rendered a revision of his work imperative.

Because of this importance of the subsequent treatment, it is necessary to record a very detailed statement of the precise operations of the present research in this particular, and to point out the differences between these operations and the methods of Stas.

Every one must agree that fusion alone is the only safe method of eliminating wholly the liquid included in the cells of the crystals, whether these crystals be produced by electrolytic or chemical reduction. The difficulty is to find an environment for the silver during its fusion from which it will not absorb or retain foreign substances.

The question presents a twofold difficulty, because both the solid support of the silver, and the atmosphere which surrounds it, must be considered. The former of these difficulties may be discussed first.

In what vessel may the silver be fused, in order to avoid contamination? Stas, in his posthumous work, recommends fusion in a cupel of basic calcium phosphate, in the flame of a blast-lamp, and subsequent ignition in hydrogen. This process, while possibly as good as he contends, may nevertheless, be a dangerous one. Every one knows the risk to a platinum crucible of igniting in it a phosphate with reducing material, and yet Stas took no steps

to prove the absence of traces of silver phosphide from the metal prepared in this way. His own observation, indeed, confirms this suspicion, for he states that silver thus fused in an oxidizing flame became covered with a yellow crystalline film, which instantly disappeared in a reducing flame. The great instability of the oxides of silver, affords reason for doubting his assumption that this film was an oxide; it seems more probable that it was a phosphate, produced by oxidation of silver phosphide, and decomposed by reduction to this compound again. Stas, relying entirely upon the superficial appearance of the silver and its flame test as a guide to its purity, would not have discovered the presence of phosphide.

The possibility of this danger is enough to incline the careful chemist to avoid the presence of phosphorus. As a matter of fact, Stas never used silver prepared in this way for his atomic weight researches;[1] and no one else seems to have used this procedure, except Scott,[2] who fused 5 grams of silver in this way for a single analysis. Of course, however, a single analysis is too slender a basis upon which to form any adequate judgment concerning its purity. Actuated by the preceding considerations, we did not take the trouble to test the method, preferring first to test others, which gave more promise of satisfactory results.

Another possible material, which has been partially tested in previous work, is carbon. Sugar charcoal may be prepared in a state very free from metallic impurities, and would serve excellently, if it were not that carbon is probably soluble to a slight extent in the molten metal. We gave this possibility a fair test, and found that when the silver is fused on a cupel of sugar-charcoal with a clean blast-lamp and moderately pure illuminating gas, it is, as a matter of fact, very pure (Expts. 67, 68, 71, on page 520). Probably the oxidizing flame used to melt the metal prevents the introduction of much carbon at first, and during the brief reducing period, in which the metal must be cooled to eliminate an excess of oxygen, there is not time to dissolve much carbon. Evidently, however, a process which depends upon the mutual elimination of opposing errors is an uncertain one, and hence not suitable for the most accurate work. That carbon is really dissolved was well shown by another experiment, in which a carbon boat, in a porcelain tube, filled with pure hydrogen was

[1] Stas, Oeuvres Compl., **3**, 75.

[2] A. Scott: *J. Chem. Soc. Trans.*, **79**, 147 (1901).

used to contain the fusing silver. This experiment yielded silver slightly less pure than the previous average; it must have contained 0.005 per cent. of dissolved carbon (Expt. 79), p. 520 (1st). Of course, however, a single experiment has but little exact weight in such a case, except to show that the process is probably undesirable.

Returning from these unsatisfactory methods to the one used very early in his career by Stas, we tested once more the use of lime as a support for the fusing silver. This seemed to be an especially appropriate substance for the containing vessel, because it is so easily obtained pure, and because it is so hard to reduce that no metallic calcium could be dissolved by the silver. But, of course, the silver must be saturated with dissolved lime; and it remained to be proved that a saturated solution of lime in fused silver is so dilute as to introduce only a wholly insignificant amount of impurity. This was easily shown by actual experiment. Ten grams of silver fused on lime were dissolved in pure dilute nitric acid in a platinum dish, and precipitated as sulphide by pure hydrogen sulphide gas, led in through a platinum tube. After filtration on a platinum funnel, the remaining liquid was evaporated to dryness in platinum. The minute trace of residue, probably due to traces of dust, on moistening with hydrochloric acid, gave no trace of the calcium bands in a spectrometer, which showed them plainly from a solution containing 0.01 mg. of lime in 1 cc. Hence it is evident, that less than this amount of lime was dissolved by the silver, *i.e.*, less than 0.0001 per cent. if any.

This experiment settled the question concerning the supporting substance, but of course, the lime must be perfectly pure. If the lime is partially made from the nitrate, it must be very thoroughly ignited before it is used, otherwise the silver may dissolve some of the oxygen caused by the decomposition of the salt. This was shown by the careful testing of a quantity of silver fused on a new boat which had not been thoroughly ignited (Expts. 72 to 76, p. 520). A boat in which pure silver has already been fused has an advantage in this respect, as well as because every accessible trace of reducible material must have been dissolved out of it. Of course, the lime used in the present experiments was especially purified, as will be related.

It is true, that even when carefully prepared, a boat of lime is likely to be so friable as occasionally to cause a partial coating of

the button of silver with the powdered lime, but the great surface-tension of molten silver keeps this all on the surface, whence it is easily dissolved by means of the dilute nitric acid always used by us to clean the metal. Scott, who has objected to the use of lime, again on the basis of a single experiment, does not mention having taken this necessary precaution.

All the silver used in the three final series of experiments which follow, was thus ignited in pure, well-seasoned lime boats, capable of holding from 30 to 50 grams at each fusion. The unglazed porcelain boats in which the lime was moulded were made on purpose for this object by the Royal Berlin Porcelain Manufactory.

The environing atmosphere around the silver during fusion next claims attention, since that, too, may vitiate the molten metal. Obviously air is impossible. A vacuum seemed *a priori* to be the best means of preventing the access of impurity, but to our surprise, we found that silver fused in a vacuum was sometimes less pure than that fused in the open flame of the blast-lamp (Expts. 72 to 76, p. 520). This puzzling circumstance was ascribed finally to the supersaturation of silver with oxygen, derived either from included silver nitrate or from the calcium nitrate in the boat.[1] Silver precipitated by formate and ignited on a pure boat, does not show this impurity, because free from oxidizing substances; and a few minutes ignition in pure hydrogen quickly removes in chemical fashion this supersaturation when it exists, thus purifying the silver. The amount of hydrogen which remains must be on the limit of the weighable, at least, we were unable to detect it quantitatively, because silver fused in hydrogen yielded exactly the same amount of silver chloride as that containing no oxygen, which had been fused in a vacuum. This is shown by the comparison of Expts. 77, 78, 80, 81, 83, and R 2 with 84, 85, and R 3. Hence Stas's conclusion, that silver does not dissolve over 0.0004 per cent. of hydrogen, is supported, although, indeed, his method of preparing the silver was somewhat different from ours, and his method of determining the hydrogen was somewhat doubtful.

The discovery of the residual trace of oxygen in the fused electrolytic metal, which had contained occluded nitrate, was not made until the work on sodium was finished, but fortunately three pieces of the silver used in that work still remained, so that it could

[1] A trace of chlorine, which, however, could hardly have been present would have had the same effect.

be compared with the purest silver which we were able to make. The comparison was made by weighing the chloride obtainable from known weights of each sample, and the details will be recorded in full in the chapter concerning the synthesis of this salt. For the present, it is enough to say, that the silver used in the work on sodium yielded 0.004 per cent. less chloride than the purest silver,[1] and, therefore, was assumed to contain that percentage of impurity. A change of only 0.002 in the atomic weight of sodium was caused by this difference.

All the silver used in the final series of syntheses of silver chloride was free from dissolved oxygen, and three of the specimens must have been free from hydrogen also. The method of treating each is sufficiently specified in the table of results, and need not be further discussed here. The silver used in this part of the work was the purest we were able to prepare, and we know of no impurities which it could have contained, except in some cases, the insignificant trace of hydrogen already mentioned.

The boat used for the fusion was made from a mixture of pure lime and calcium nitrate, and was contained in a porcelain tube, closed with Hempel stoppers. The tube was heated to bright redness in a Fletcher furnace.[2] The resulting bars of silver were freed from the adhering lime by scrubbing with *clean*, hard sand, and successive treatments with dilute nitric acid. The silver nitrate was dissolved away by ammonia, and many washings with water were followed by drying the bar in a hard glass tube, at about 400° in a vacuum.[3] Water might otherwise become sealed into the microscopic cavities, often present in fused silver, during the next operation of cutting into blocks. The cutting is best carried out upon a silver plaque by means of a clean, steel cold chisel. The blocks thus cut were superficially etched once more with nitric acid, so dilute that a possible trace of iron could not assume the passive state, and the cleansing and drying operations were repeated. The pieces then preserved in a desiccator over potash are ready for weighing and analysis.

After the details of the analysis have been discussed, the relation of the purity of this silver to that of Stas, will be made clear.

[1] The average of analyses 65, 66, 70 were compared with the average of the final series (see pp. 520 and 524).

[2] *Proc. Am. Acad.*, **30**, 379 (1895).

[3] The silver used in R 1, R 2, and R 3 (pp. 520 and 524) was wrapped in pure silver foil during this ignition to prevent contact with hot glass.

Lime.—The preparation of pure lime upon which to fuse the silver, was a matter of great importance, because of the danger that any impurity in it might contaminate the silver. Its preparation was begun by dissolving marble in nitric acid, boiling with an excess of calcium hydroxide, filtering, neutralizing, and twice recrystallizing the calcium nitrate.[1] Calcium carbonate was then precipitated with ammonium carbonate, repeatedly washed, and finally dissolved in redistilled nitric acid.

The resulting nitrate, made alkaline with ammonia, was electrolyzed to remove a suspected trace of iron, and filtered through a layer of calcium carbonate upon a Gooch crucible. It was found that ammonium carbonate, of variable composition, could be conveniently distilled with steam from its solution. With such a distillate, prepared wholly in platinum, calcium carbonate was again precipitated, and well washed. A small portion of this was converted into nitrate.

Ignition of the calcium carbonate to oxide was carried out in porcelain, since platinum is slightly volatile at high temperatures, and might have contaminated the lime. A dry mixture of calcium oxide with about a fifth its weight of powdered anhydrous nitrate was packed into specially made large, unglazed boats of Berlin porcelain. The moulded mixture, when heated to redness, sintered firmly together, and made a chemically pure receptacle, large enough to contain about 50 grams of silver at a time. In order to prevent adhesion of the boat to the glaze of the porcelain tube, the boat should not fit the tube very closely, and it is well to cover the glaze under the boat with a layer of pure, powdered lime.

Utensils.—Of course, all the containing pieces of apparatus, dishes, funnels, crucibles, retorts, condensers etc.,—were of platinum, wherever silica was to be feared, and platinum was not itself harmful. In this latter case, either silver vessels were used, or vessels of the best insoluble glass (Jena, or "non-sol,") or porcelain or in some cases fused quartz were used. In this way, the greatest possible purity of the preparations was assured.

The Solubility of Silver Chloride.

Mulder pointed out, in 1857,[2] that the solubility of silver chlo-

[1] Calcium nitrate should be recrystallized below its transition temperature, 44°, a proceeding much facilitated by inoculation with the respective hydrate.

[2] Mulder: "Die Silverprobirmethoden," Leipzig, 1859.

ride is sufficient to affect all quantitative results into which the precipitation of this substance enters. Stas overlooked this solubility in his early determinations, and hence in 1876, repeated some of them.[1] Other more recent experimenters[2] have, in general, confirmed Stas's later conclusions about this solubility, so that it is not important here to give a lengthy statement of our further confirmatory results.

There can be no doubt that freshly precipitated silver chloride is soluble in cold water to the extent of several milligrams per liter, and that this solubility steadily diminishes, without a very sharp change at any time, as the precipitate remains in contact with the liquid.

A variable solubility of this nature may be due to one of two causes: either the precipitate is capable of assuming two or more allotropic forms, of which the least stable appears at first,[3] or else it separates in a finely divided state, and gradually becomes aggregated into larger masses. The work of Ostwald[4] and of Hulett[5] has shown how greatly a difference in size of the grains may affect the solubility, especially of a salt only slightly soluble.

The latter explanation seems the more probable, for several reasons. In the first place, no sharp change in the solubility has ever been detected, such as would be expected from the appearance of a new, more stable solid phase. Again, the difference between the specific gravity of the flocculent precipitate and fused horn-silver is very slight, and their heats of solution in cyanide are identical, indicating little or no difference of molecular constitution between the two.[6] Moreover, as will be shown later, the curdy precipitate may be successfully washed in a measure unattainable with crystalline powders, showing that the innermost recesses of the solid are more than usually accessible, and therefore, that the structure is very finely divided and loosely knit. The more compact, less soluble precipitate, obtained either by heating or by long standing, has largely lost this possibility of being thoroughly washed, and has become also much less soluble

[1] Stas, Oeuvres, **1**, 751.

[2] For references see Böttger: *Ztschr. phys. Chem.*, **46**, 189 (1903); Richards: *Proc. Am. Acad.*, **29**, 69 (1893).

[3] Ostwald: *Ztschr. phys. Chem.*, **22**, 307 (1897).

[4] Ostwald. *Ibid.*, **34**, 495 (1900).

[5] Hulett: *Ibid.*, **37**, 385 (1901); **47**, 357 (1904).

[6] Laevinsohn determined the specific gravities. *Ztschr. phys. Chem.*, **42**, 353 (1901). His results were verified, and the thermo-chemical argument added to them by Dr. W. N. Stull and one of us, in some work not yet published.

—facts quite in line with the above hypothesis. However, this may be, the uncertainty of the solubility is a fact of important significance to the analyst, for it obliges him to determine the amount in solution in every experiment—the solubility can never be assumed as known.

The matter is yet further complicated by the well-known fact, that the presence of excess of either ionized silver or ionized chlorine causes a depression of the solubility, in the manner demanded by the law of concentration effect.[1] A large excess of either precipitant reduces the solubility to so small a value as to be practically negligible in most cases.[2] This may, indeed, be the reason why the precipitate appears in a form so loosely knit, for at the moment of precipitation it is almost impossible that the two precipitating liquids should for more than an instant be exactly equivalent, hence each first particle of precipitate would quickly be surrounded by a liquid unfavorable to its union with another in compact crystalline fashion.

Mulder thought that an excess of either silver or chloride equivalent to four times the weight of the dissolved silver chloride was enough to complete the precipitation, and Stas thought that exactly three times the equivalent amount sufficed. It is clear now that this limit is determined merely by the efficiency of the means used to detect the last faint cloud of precipitate, and then only approximately.

As has been said, the changing solubility demands that every filtrate be tested quantitatively. The methods which may be used are all of them open to some criticism. The determination of electrolytic conductivity is in vain when any other electrolyte is present, and its interpretation is complicated, even in pure, aqueous solution, by possible hydrolytic complications; the determination of electromotive force depends upon the rigorous application of the law of concentration effect to electrolytes—a somewhat doubtful question; the actual evaporation of the solution and weighing of the precipitate leads to many errors when silver is in excess,[3] and the determination of the intensity of the opalescence upon precipitating the dissolved chloride depends greatly on the details of the production of the opalescence.

From among all these methods, we chose the last, after a very

[1] Hoitsema: *Ztschr. phys. Chem.*, **20**, 272 (1896).
[2] Compare page, 486.
[3] Richards: *Proc. Am. Acad.*, **29**, 71 (1893).

careful study of their probable errors. But although fairly confident of its results, for reasons shortly to be given, we were careful in every case to allow in each experiment as little dissolved silver chloride as possible, so as to reduce the possible error to a minimum.

The method of comparing the intensity of the cloudiness of opalescent solutions, and therefore, the quantities of suspended precipitate has already been discussed, at some length, in a recent paper on the nephelometer.[1] This instrument consists of a device for the comparison of the tint or brightness of two solutions containing precipitate, viewed against a dark background. By making one of these opalescent mixtures from a known amount of material an unknown amount may be estimated by comparison with it. It is easy to show that with this instrument the average of many results is within 1 or 2 per cent. of the truth, so that the error with 2 mg. of dissolved silver chloride is probably less than 0.04 mg. This degree of accuracy is as great as can be attained in the collection of a precipitate for weighing, hence the method is to be ranked among those suitable for exact work.

With the perfected nephelometer it was possible to study the progressing precipitation of a very dilute silver chloride solution in a way previously impossible, and several unexpected irregularities were found during its course. Since these are important in the quantitative sense, they must all be briefly discussed.

The most striking of these is the variation in the time of complete precipitation caused by the presence of electrolytes. For example, a solution of silver chloride on adding a slight excess of soluble silver salt becomes opalescent far more quickly in the presence of much sodium nitrate or nitric acid than in the absence of such an electrolyte. At the end of five minutes the former solution appears about three times as cloudy as the latter; and several hours are needed for the two solutions to attain equality of opalescence at a maximum value, which thereafter remains constant. It appears from this fact that the precipitate probably at first forms in a colloidal state, since electrolytes are known to hasten the precipitation of colloids. This inference is confirmed by the occasional appearance of pale blue or pink tints in the incipient precipitate, which disappear as the cloudiness becomes more intense.

[1] Richards and Wells: *Am. Chem. Jour.*, **31**, 235 (1904).

Oddly enough, a solution of pure silver chloride (made by shaking the curdy precipitate with water and filtering) attains its maximum cloudiness after subsequent addition of silver nitrate more rapidly than a solution of similar dilution made by mixing equivalent amounts of very dilute silver nitrate and sodium chloride solutions. The trace of sodium nitrate left, in the latter case, seems to be unable to counteract some other tendency holding the precipitate in solution. At first it seemed possible that minute, invisible "crystal germs" might be present in the filtered solution, which accelerated the appearance of the opalescence, but this surmise was soon overthrown experimentally. A solution made from curdy silver chloride, and found nephelometrically to contain 1.28 mg. per liter, was diluted with an equal bulk of pure water, and its concentration, after agitation for over one hour, was determined by the nephelometer. The average concentration found by five trials, 0.61 mg. per liter, agreed with that expected within a reasonable limit of error, and moreover, the speed of precipitation was no less than before. There could hardly have been any "crystal germs" existing in the more dilute solution, hence one must assume that the undissociated part of the silver chloride is really in a different state when it is dissolved out of salt long formed, from that in which it is when in the act of precipitation. The observation at least adds one more anomalous fact, perhaps giving a clue to some of the other anomalous facts, concerning the solubility of silver chloride.

The application of these observations to the nephelometric analysis of a very dilute silver chloride solution is obvious. It is a difficult matter to prepare a standard, which will behave in exactly the same way as the solution to be estimated. By adding appreciable quantities of nitric acid to each, it is possible, however, to hasten the precipitation of each so greatly as to cause them to proceed at a speed almost equal; and the maximum cloudiness thus quickly attained persists unchanged in relative intensity for hours. It seems highly probable that the result thus reached really represents the amount of dissolved silver chloride; especially, because the same result is attained after a much longer time, even when no electrolyte is present.

The actual extent of the solubility of silver chloride thus estimated varied through wide limits, as has already been stated. For the solution freshly filtered from the curdy precipitate in the

usual condition at 20°, the amount dissolved was ordinarily about 1.5 mg. per liter, a result about equal to that of Kohlrausch and Rose and others. On long standing, such a solution was found to decrease in concentration, on one occasion, to as little as 1.1 mg. per liter, although no visible precipitate was seen on the glass. The trace of material represented by this difference was probably adsorbed by the glass. This observation points out the necessity of determining the strength of an unknown solution immediately after its filtration—a precaution which was carefully heeded in the quantitative part of the work.

Although sodium nitrate and nitric acid hasten the precipitation of the curdy opaque form of silver chloride, they augment slightly the amount which finally remains in solution. By means of the nephelometer, it was found that a saturated solution of curdy silver chloride in the presence of about tenth-normal sodium nitrate and a small amount of nitric acid usually contained as much as 3 mg. of the slightly soluble halide per liter. A mixture of this type was present at the conclusion of each nephelometric experiment recorded in the experiment on the ratio between sodium chloride and silver, and the bearing of the actual value on the investigation will be there discussed.

The solubility of silver chloride in a liquid containing a large excess of one of its ions has been stated to be "practically negligible in most cases" (p. 483). In determining the ratio between silver and silver chloride, however, it seemed advisable to determine even this solubility, which may partly represent the solubility of the undissociated silver chloride, as distinguished from that ionized, and also includes the slight correction for the imperfect retaining power of even the best filters.

The fact that a single part of silver chloride may be detected in 30,000,000 parts of water by the nephelometer, in the presence of an excess of silver nitrate, shows the approximate order of this solubility.[1]

In five experiments, in which silver chloride was precipitated by an excess of hydrochloric acid, the combined mother-liquor and wash-waters remaining after filtration were evaporated to dryness. The residue was taken up with a very small quantity of ammonia, and then neutralized with nitric acid. After the addition of a slight amount of sodium chloride, the silver chloride

[1] Richards: *Proc. Am. Acad.*, **29**, 74 (1893).

was estimated by the nephelometer, by comparison with tubes made up with known amounts of silver in the same way.

	AgCl. mg.
In 3 liters	0.09
" 3 "	0.13
" 3 "	0.05
" 2 "	0.05
" 2 "	0.05
Mean	0.03 per liter.

This value represents the solubility of silver chloride in water containing sodium nitrate and an excess of hydrochloric acid, together with those traces of the substance which could not be collected upon a filter. It is not certain that the same value would be obtained if it were possible to determine this infinitesimal solubility in the presence of an excess of silver nitrate, but the fact that the limiting value previously found by one of us is about of this order seems to render this probable. Hence, for the sake of completeness, the correction was applied to the results in the latter case as well as in the former, although it was so small as not even to affect the third decimal place of the atomic weight of sodium.

Further consideration of the solubility of silver chloride will be given in other appropriate places.

THE OCCLUSION OF DISSOLVED SUBSTANCES BY SILVER CHLORIDE.

It is well known that all precipitates have a tendency to carry down with them other substances from the solution in which they are formed.[1] According to the nature of the precipitate, the mechanism of this contamination varies. A basic precipitate such as ferric hydroxide is likely to carry down traces of acid in the form of basic salt; an acid precipitate such as silica is likely to carry down traces of base; many substances are contaminated in the act of precipitation by the admixture of isomorphous substances in solid solution; all or nearly all crystals contain within themselves minute cells enclosing mother-liquor, and very finely divided precipitates, because of their large surface, pertinaciously adsorb in varying amount impurities from the supernatant solution. Obviously, contamination from any of these sources must

[1] Jannasch and Richards: *J. prakt. Chem.*, **39**, 321 (1889); Schneider: *Ztschr. phys. Chem.*, **10**, 425 (1892); Richards: *Proc. Am. Acad.*, **35**, 377 (1900); *Ztschr. phys. Chem.*, **46**, 189 (1903).

be scrupulously avoided in accurate work, and the peculiar qualities of each precipitate, under investigation, must be studied.

As has been said, silver chloride was known by Stas to occlude silver nitrate, which is easily detected by its blackening effect upon fusing the contaminated chloride.[1] This test is a very delicate one. Stas found that upon working with solutions of silver nitrate weaker than decinormal, the occlusion was so slight as to be negligible; therefore, in his early experiments he took great pains never to use solutions stronger than this. Later he seems to have overlooked this precaution, since he used much more concentrated solutions. Although realizing that silver nitrate is occluded by the precipitate, Stas seemed never to have guessed that other salts might also be taken up in this way. Evidently, the question was one which needed further investigation; and the outcome of the investigation is recorded below.

It was convenient at first to determine whether or not the occlusion of sodium nitrate or sodium chloride would also affect the appearance of the silver salt on fusion, in order to discover an easy qualitative test for the presence of either. As a matter of fact, the former salt was found by actual admixture to color the fused silver chloride a pale buff, rendering it opaque, while the latter had no perceptible effect upon its appearance. Thus Stas could not have detected the presence of sodium chloride in his precipitate by the appearance, whether fused or unfused. An impurity of silver nitrate being thus the most easily detected among the possible impurities, the next step was to use the contamination with this salt as a means of testing the properties of the precipitate.

It was early found that upon shaking pure silver chloride with a solution of silver nitrate, the latter is adsorbed upon the surface of the precipitate. If a solution containing silver nitrate and the curdy precipitate is divided into two equal volumes, one containing the precipitate and one clear, and if the precipitate is then carefully washed, more silver nitrate will be found in the portion which contained the precipitate than in the other portion. A further evidence of this adsorption is found in the fact, that the theoretical amount of washing is especially inadequate to remove the last traces of adhering electrolyte.

[1] Richards: *Proc. Am. Acad.*, **29**, 76 (1893). The blackening occurs in full measure only when the silver nitrate is occluded from aqueous solution. Perfectly dry silver nitrate fused with dry chloride is but slightly decomposed, and the fused mass is merely gray, not black. The probable explanation is obvious.

These experiments show not only that the nitrate is adsorbed, but also that some at least of the adsorbed salt may finally be washed off.

In view of this result, it seemed probable that the reason why silver chloride occludes silver nitrate in the act of precipitation, is because the former adsorbs the latter during this process, and the adsorbed material is then covered up by newly formed precipitate. The more dilute the precipitating solutions, the less considerable would be the adsorption.

The peculiar curdy, flocculent form of this precipitate suggested that since the material is so flexible, long standing and gentle agitation with pure water might allow the occluded material to escape, although from a more rigid precipitate, this escape is known to be impossible. With this possibility in view, a number of experiments were made in the following manner. Silver chloride was precipitated from several portions of a concentrated solution of the nitrate, thus occluding much (in some cases as much as 0.1 per cent.) of this salt. The effort was then made to wash these precipitates, and the possibility of thorough washing was found to vary greatly with the treatment of the precipitate. In those cases where the precipitate had remained for two or three days in contact with a mother-liquor rich in silver, it was found much more difficult to remove the silver than in cases where the washing was more prompt. It seems as if the innermost cells of the precipitate are closed upon standing, during the well-known contraction which then occurs. In one case where normal solutions had been used in precipitation, six prompt, gently agitated washings with pure water were enough to remove practically all the occluded material, and yield a chloride, which fused without blemish; but this praiseworthy behavior was the exception, rather than the rule. In this case, the innermost cells must have been cleaned before they closed during the compact aggregation of the precipitate, but usually traces of silver nitrate were enclosed, and when once enclosed, were beyond the reach of even a dozen washings.

Therefore, more dilute solutions of silver nitrate were used in precipitating, in order to find the limit beyond which a satisfactory precipitate was certain. Third-normal solutions were found to be still slightly too concentrated, but fifth-normal solutions always yielded a satisfactory result, if speedily, but gently, washed six

times, and then occasionally agitated in pure water in order to dissolve out the last trace of nitrate. In previous determinations in this laboratory, still less concentrated solutions (tenth-normal) were used, so that no correction need be applied to those determinations on this account.[1] This further dilution is necessary unless the curdy precipitate is speedily washed, or agitated with a solution containing no excess of silver.

Having thus obtained light on the mechanism of the occlusion of silver nitrate, we turned our attention to the possibility of occluding sodium chloride. Here, as had been said, no qualitative experiment can conveniently prove the presence of the impurity. Hence recourse was had to a quantitative experiment. An amount of pure salt, known by previous experiment with very dilute solutions to be exactly equivalent to a given weight of pure silver, was carefully weighed out, and the solid dropped into a fairly concentrated solution of the nitrate, according to Stas's later method of procedure. After two hours' thorough shaking and a day's standing, which Stas had always given, it was found that 0.014 per cent. more of salt had to be added in order to attain exact equivalence, showing that this amount of salt remained occluded by the precipitate, even after the shaking and standing. Agitation for another day leached out about one-half of the occluded salt, but seven days' soaking and agitation were required before the full amount (0.014 per cent.) of extra silver nitrate was needed to attain equivalence with the sodium chloride dissolved out of the precipitate. Subsequently in several days no more salt appeared, hence the final condition must have been reached. Since probably some silver nitrate also was occluded, it is clear that these figures represent a minimum value, and the certain error introduced by Stas's method of procedure was demonstrated. The reason why he obtained consistent results, was simply because he used exactly the same method in each analysis.

Obviously, then, a solid salt is not to be dropped into a precipitating solution—indeed, such a proceeding is so repugnant to the instinct of a precise quantitative analyst, that it is surprising Stas should have been guilty of it. But how dilute must the precipitating sodium chloride be in the present case in order to avoid the danger? Careful experiments showed that with fifth-normal solutions, as in the case of silver, such slight occlusion as existed was

[1] See for example, Richards: *Proc. Am. Acad.*, **29**, 76 (1893).

quickly removed by gentle agitation, and after a short time the mixture showed a constant equilibrium point. Hence, in our final experiments the solutions were never essentially more concentrated than this. In previous similar work in this laboratory, the solutions of halide were rarely stronger than fifth-normal, and never much stronger, so that the error from this source must have been very small.

It might be supposed that when the sodium chloride and silver nitrate are too dilute to be carried down with the precipitate, sodium nitrate is not likely to be carried down in important amounts, for if both silver and chloride are fifth-normal, the resulting sodium nitrate must be tenth-normal, a dilution at which even silver nitrate is not sensibly occluded. Nevertheless, as a matter of fact, the final experiments yielded quantitative evidence of the occlusion of a trace of this salt, amounting to 0.005 per cent. of the weight of the precipitate. This is probably because the precipitate was obliged to stand for some time in the solution, and it is doubtful if this source of error could be wholly avoided.

From these experiments it appears that the degree of dilution at which occlusion ceases to be seriously troublesome is about the point at which most physical chemists agree that the realm of dilute solutions begins. Hence it would seem that in these cases of adsorptive occlusion the undissociated salt is that which is occluded, in confirmation of other work.[1]

Obviously the occlusion of silver nitrate, or of sodium chloride, would affect the results of the analysis, no matter whether silver or silver chloride served as the weighed standard wherewith to compare the weighed sodium chloride, although more seriously in the former case than in the latter. On the other hand, the occlusion of sodium nitrate could only affect the result when the silver chloride was weighed; its occlusion would have no effect on the amount of silver required to precipitate the chlorine. The possible effect of these disturbing influences will be alluded to again during the recital of the quantitative operations.

It is needless to say that these experiments were carefully carried on in complete darkness in order to avoid the known disturbing effect of photochemical action. The temperature was usually 20° C. Undoubtedly this condition is important, since

[1] Richards, MacCaffrey, and Bisbee: *Proc. Am. Acad.*, **36**, 477 (1901).

the aggregation of silver chloride is greatly affected by change of temperature.

The Ratio of Sodium Chloride to Silver Chloride.

Two obvious means are available for determining the combining weight of sodium chloride—one, by weighing the amount of silver chloride which may be made from a given weight of this salt; the other, by discovering the weight of silver needed to precipitate all its chlorine. Both these methods involve a consideration of all the special points mentioned in the preceding sections, and both are essentially gravimetric, although both involve the use of the nephelometer in order to estimate the last traces of silver or chlorine in the supernatant liquid.

The actual investigation of these two methods proceeded simultaneously in order to economize the time during the long delays to which each was frequently subject. Indeed, in some of the previous work in this laboratory, where the pure materials were scarce, the two methods were actually combined in the same analysis, by first determining the weight of silver needed to precipitate the chloride, and then weighing the chloride produced. This last procedure is nevertheless somewhat objectionable on account of its complication. It is, moreover, subject to slight opposing errors; the avoidance of one of these involves the admission of the other, as has already been pointed out in a preceding communication.[1] The magnitude of the uncertainty thus caused is not great, and the final error involved is insignificant even in atomic weight investigation of ordinary caliber, usually not exceeding 0.01 per cent; but in the present case extraordinary accuracy was sought. Hence, although the methods were studied simultaneously, they were never combined in the same analysis. For this reason the work is easily divided into two sections, each treating one of the two ratios named above. Of these it is convenient to discuss first the ratio of the chlorides to one another; and this discussion is taken up in the present chapter.

After the preliminary experiments had indicated the nature of the problems involved, a single specimen of pure sodium chloride was used for analysis until all the details of analysis were perfected. Then the various samples of salt were analyzed by methods of known precision. The temptation to vary two conditions in a

[1] Richards and Archibald: "On the Atomic Weight of Caesium." *Proc. Am. Acad.*, **38**, 443 (1903).

single new experiment is thus easily avoided. The detailed description of every step of the analytical process follows.

It was soon found that salt when free from excess of acid can be fused in a platinum crucible in the air without either attacking the crucible to an important extent, or becoming appreciably alkaline. Quantitatively, it was later proved, as will be shown, that salt thus prepared is identical to that fused in a platinum boat in a vacuum and transferred and weighed in the familiar "bottling apparatus "which has served so conveniently for hygroscopic substances. It was found, moreover, that a crucible full of salt thus prepared did not gain in weight during the operation of weighing, on account of the dry winter atmosphere of the steam-heated weighing-room. Probably this would not have been the case in a moist climate; but being the case, it facilitated greatly the present work.

The crucible generally used for fusing the salt was, of course, previously freed from iron, and during twenty-three fusions it lost only 0.47 mg., or 0.02 mg. each time. It is possible that a portion of the weight was lost by volatilization during the preliminary ignitions of the crucible, when it was being prepared for weighing alone; but probably most of this trace of platinum went into solution in the salt. The weight of the crucible before fusion was always taken as the true one, however; therefore even this slight possibility of loss of course could not affect appreciably the quantitative result.

During the fusion of the salt the crucible was enclosed in a larger covered Berlin porcelain crucible, especially made to fit it, and heated by a blast-lamp in a small clay furnace. The products of combustion were suitably deflected, so that only pure air should be in contact with the salt in the crucible. The fused salt was cooled in a desiccator in the balance-room, and the weighing was conducted by the substitution of a suitable tare-crucible, as usual.

In order to avoid all risk of accidental loss the salt was dissolved from the crucible by placing it in a large covered beaker, and after covering it carefully with water, agitating it gently from time to time until solution was complete. This solution thus carefully prepared was transferred to a 2-liter Erlenmeyer flask with a well-ground glass stopper where it was diluted to suitable volume (about 5 liters per mol). Here it was precipitated by

at least equally dilute silver nitrate in excess. The precipitate was freed from the supernatant mother-liquor by filtration as soon as it had cleared enough to make this separation possible. Promptness is needed in order to avoid the permanent occlusion of sodium and silver nitrate in the manner already stated, but too great promptness prevents complete precipitation of the silver halide. About fifteen hours was usually allowed for the settling of the solution. Agitation is not necessary.

The clear supernatant liquid was decanted through a large, carefully prepared Gooch crucible. The mat of this Gooch filter, through which all the mother-liquor and wash-waters were passed, was made of selected fibrous asbestos shreds, which had been boiled with nitric acid and well washed. The mat was a trifle thicker than a filter-paper—so that the holes of the crucible were indistinctly visible, when viewed in front of a strong light—and was not allowed to extend up the sides of the crucible. A preliminary ignition of the mat was found to result in a slight disintegration and brown coloration, and caused loss during washing; therefore before weighing, the mat was dried at a lower temperature, namely, about 150°. This same temperature was used later in drying the silver chloride. During the operation of washing at first all but a trace of the precipitate was left in the flask, and it was then rewashed by decantation. After each washing the precipitate was allowed to drain several minutes, for silver chloride is known to hold water like a sponge. At the second or third washing a disintegration of the precipitate often took place, resulting in an emulsion-like mixture, but in most cases this could be prevented by the presence of a little nitric acid. The precipitation had been made with silver nitrate in excess. The first three washings of 0.2 liter each were made with very dilute silver nitrate, and this was displaced in the fourth washing by about 0.05 liter of pure water. In such wash-waters, which, with mother-liquor, usually amounted to about 2 liters, no trace of chloride could be found by the nephelometer. The main weight of silver chloride was corrected by +0.06 mg., however, in every case, for the otherwise determined solubility in such wash-waters. From five to eight subsequent treatments with pure water, very slightly acid, in 0.1 liter portions, completed the washing. These later wash-waters were treated in the manner described below, in order to determine the chloride which they always contained.

The precipitate was now transferred to the filtering crucible wholly by means of a stream of water. It was found convenient, first to transfer and pack down by air pressure a small portion of the precipitate on the asbestos mat, in order that the greater part of the silver chloride might be easily separated from this mat for fusion. By resting the lip of the flask on the Gooch crucible it is possible to direct a stream of water from a wash-bottle into the flask and finally wash out every particle of precipitate. In the most careful experiments the wash-bottle was provided with protecting bulbs to preserve the purity of the water, or was dispensed with altogether, being replaced by a jet driven by hydrostatic pressure. At this stage the cloth covering was necessarily removed from the flask. The flask was finally rinsed with ammonia, which was carefully tested for a possible trace of silver chloride.

On drying the precipitate the temperature was made to rise very slowly above 100° during two or three hours. This deliberate drying was found to be more effective than the immediate application of high temperature, presumably because a hard coating was not then formed about the mass of the precipitate. Finally the temperature was maintained at about 150° for two or three hours longer. In this way fairly constant weight is easily attained, which fifteen hours further heating at 150° changes very slightly. The last traces of water were always expelled by fusion, as is described below.

In many of the experiments the silver chloride was dried in an electric drying oven heated by hot platinum wires, conveying a current of an ampere or two.[1] When properly constructed this oven gives very satisfactory results. The working of the oven is somewhat more satisfactory if the platinum wires are not heated to redness. In some of the later experiments the precipitate was dried in a clean copper oven heated by a gas flame with no apparent difference in result.

The precipitate thus collected and dried was carefully weighed and then freed from adhering asbestos and transferred to a weighed porcelain or quartz crucible for fusion. The crucible and contents were tared against a similar crucible and contents, and the silver chloride under examination was then fused in a clean oven constructed from a large porcelain crucible, from the interior of which the products of combustion of the gas were carefully deflected.

[1] Richards : *Am. Chem. J.*, **22**, 45. 1899.

The fusion is necessary, because minute drops of water are always held by the hardened silver chloride in sealed cells. It is true that the loss on fusion is not great, never amounting to 0.01 per cent. of the weight of the precipitate, but it was enough to receive consideration. In every case it was determined and the appropriate individual correction applied to each weight. The maximum value of the correction was 0.008 per cent. and the minimum 0.003 per cent. That the loss was not due to volatilization of silver chloride is easily shown by the invariability of the weight upon fusing a second time. That it was not due to accidental reduction was shown in the later experiments by fusing again in a stream of chlorine, when the mass gained on the average only 0.001 per cent. The fused silver chloride, even before its treatment with chlorine, was usually pearly and colorless.

In any case it is clear that this loss on fusion, which has been rejected as of doubtful significance by some authors,[1] really represents included water, and must be heeded.

The determination of the weight of the main mass of the precipitate having been thus determined, attention must be directed to several other precautions necessary to insure exact work. In the first place, all the liquid which has passed through the Gooch crucible was passed through a small washed filter, in order to collect the minute asbestos shreds which even the best fibrous asbestos seems to lose under pressure. This was done as soon as possible after filtration and before proceeding to the solubility determination. A siphon filtering arrangement, or a large inverted flask fitted with a carefully cleansed rubber stopper with two tubes arranged so as to maintain constant level, obviated the tedious process of filtering by hand. The little filter was finally washed free from salts, and the weight of the ignited residue (minus the filter ash) added to the weight of Gooch crucible and precipitate. This residue usually amounted to only 0.1 or 0.2 mg. Observation in the microscope easily showed that the residue was really asbestos.

Because it was the object of the research to test every step of the processes involved, the loss and recovery of asbestos shreds was tested by special blank experiments. Large volumes of water were passed through empty Gooch crucibles provided with the usual mats; and the loss of each crucible after drying was found,

[1] Scott: *J. Chem. Soc. Trans.*, **79**, 147 (1901).

as well as the weight of shreds recovered from the filtered water. Below are given the results of these blank experiments:

	Loss of crucible.	Asbestos found.
1	0.00034	0.00034
2	0.00016	0.00045
3	0.00019	0.00016
Average	0.00023	0.00032

In two of these experiments the loss very nearly equaled the amount of asbestos found; the other one must have been contaminated by an accidental outside impurity; but the results of the blank experiments are enough to show that the correction is a real one and not to be omitted.

In most experiments the residue of asbestos shreds was found after ignition to contain a trace of silver. This was undoubtedly produced from the decomposition of silver chloride during ignition, the latter salt having passed through the Gooch as exceedingly fine particles or having precipitated, in time, upon the asbestos shreds. The amount of this silver, as well as the amount of asbestos shreds, varied according to the efficiency of the Gooch mat and the fineness of the holes of the Gooch filter—the smaller those holes the better. The loss of chlorine upon ignition was determined in sixteen experiments, chiefly in those upon the synthesis of silver chloride. This was done by determining the trace of reduced silver by Volhard's process, using 1/100 normal solutions. The average of determinations, which varied from 0.00 to 0.07 mg., amounted to only 0.02 mg. This correction was applied. Although negligible, its magnitude had to be determined in order that one might be assured of safety in neglecting it.

With the asbestos at our disposal, the prepared Gooch crucible was not at all hygroscopic. An hour's standing in the balance-case had no effect upon its weight. Even upon ignition the mat, weighing less than 0.03 gram, lost only a negligible amount—and it was never heated above 150° in the actual analyses.

As has already been said, no chloride could be found by the nephelometer in any of the wash-waters containing any considerable amount of silver nitrate. Hence, after filtration through the small filters, these were cast aside and the small solubility correction of 0.03 mg. per liter applied to them.

The next two or three wash-waters containing only small

amounts of nitrate were collected separately, because they contained traces of chloride also. The subsequent wash-waters, free from nitrate, but containing much chloride, were all united. The chloride in both separate portions was carefully determined by means of the nephelometer—that is, by comparison of opalescence. The two portions, one containing traces of silver nitrate and one free from salt, must be estimated separately, because if all the wash-waters are mixed together the opalescence usually occurs prematurely, a circumstance which interferes with the accuracy of the nephelometric comparison.

The amount of silver chloride thus found in the wash-waters was added to the weight of that collected on the Gooch crucible.

Any accidentally included foreign substance—for example, silica from the glass-stoppered flasks, dust from the air, or occluded sodium nitrate—which would make the obtained weight of silver chloride too great, would make the computed atomic weight of sodium too low. Since our results were lower than Stas's, particular attention was paid to these and similar possibilities. One question especially seemed to demand an answer, namely, that concerning the possibility of the abrasion of powdered glass from the ground-glass stopper of the precipitation-flask.

A newly ground stopper sheds glass noticeably. It must always be polished and rubbed a long time until the loose particles are thoroughly dislodged. A flask of soft glass never ceases to grind away slightly every time the stopper is inserted. The large 2-liter Erlenmeyer flasks used in the final experiments were of very hard insoluble glass, with rather wide necks, very suitable for precipitation and for washing. In order to test the extent of their abrasion, one of the stoppers was removed and replaced a hundred times. The resulting powdered glass was collected on a small, fine filter and found to weigh 0.2 mg. Since, during a single determination, the stopper was not replaced over a dozen times, it is safe to infer that the error from this cause could not have exceeded 0.02 mg.—a negligible quantity.

Other sources of contamination were so carefully guarded against that they can hardly have been present.

The foregoing general description may be profitably illustrated by recounting the details of a single experiment, before the results of all the experiments are given.

EXPERIMENT 63. APRIL 5, 1904. SALT J.

	Grams.
Corrected excess weight of crucible over counterpoise	0.19994
Corrected excess crucible plus fused salt over counterpoise	5.76754
Weight of salt in air (24°, 764 mm.)	5.56760
Vacuum correction	+0.00231
Weight of sodium chloride in vacuum	5.56991

As a suitable excess of silver nitrate, 16.40 grams were taken for precipitation. The concentration of the silver salt being about fifth-normal and that of the sodium salt not much greater, the total mother-liquor was 1.4 liters. Five washings of the precipitate were made after it had stood over night, with 0.2 liter portions of water containing about 0.05 gram of silver nitrate per liter. Washings 6 and 7 were made with pure water and collected separately. Washings 8 to 12 were made with slightly acidified water and collected separately. The whole precipitate was finally washed upon the Gooch crucible. After drying, it appeared perfectly white.

	Gram.
Corrected excess weight Gooch crucible (dried at 150°) over counterpoise	0.21709
Corrected excess weight crucible and AgCl (dried at 150°) over counterpoise	13.87382
Weight of silver chloride in air	13.65673
Vacuum correction	+ 0.00100
Weight of unfused AgCl in vacuum	13.65773

The mother-liquors and wash-water were passed through a small filter, which was ignited in a small porcelain crucible.

	Gram.
Corrected excess porcelain crucible over counterpoise	0.42525
Corrected excess plus residue and ash	0.42535
Residue and ash	0.00010
Ash	0.00001
Residue, asbestos shreds	0.00009
Loss of chlorine during ignition	0.00001
Total residue	0.00010

A large portion of the silver chloride, 10.50 grams, was fused in a small approximately counterpoised crucible weighing about 8 grams.

Corrected excess crucible plus AgCl over counterpoise[1]	10.64846
After fusion, corrected excess over counterpoise	10.64769
Loss of 10.50 gram. AgCl on fusion	0.00077
Hence loss of total AgCl $= \frac{13.66}{10.50} \times 0.00077 =$	0.00100

The nephelometer revealed no chloride in the mother-liquor and first five washings; the correction of +0.07 mg. was applied for this solubility even in the presence of the excess of silver nitrate.

Washings 6 and 7, volume 220 milliliters in all, were found to have a trace of chloride, and its amount was estimated by the nephelometer, making comparison with two different standard tubes.

The factor for converting 1 milliliter of standard solution in a nephelometer tube into silver chloride per liter was 0.047.

Standard tube contained NaCl solution.	Time of forming opalescence.	Heights of opalescences appearing equal.		Ratio of heights.	Soluble silver chloride.
		Standard.	Wash-waters.		
cc.					
0.02	15 min.	30	100	0.30	$0.30 \times 0.02 \times 0.047$ = 0.00028 gram per liter
0.005	7 min.	100	80	.....	.....
.....	9 hours	100	85	1.18	$1.18 \times 0.005 \times 0.047$ = 0.00028 gram per liter

For 220 cc., the weight of dissolved AgCl is $\frac{220}{1000} \times 0.00028 =$ 0.00006 gram.

Similarly for washings 8 to 12 (0.94 liter) was found on the average 0.00146 gram of silver chloride per liter (the individual determinations being 1.47, 1.41, 1.54 and 1.44 mg.)

For 940 cc. we have $\frac{940}{1000} \times 0.00146 =$ 000137 gram,	
and hence the total dissolved silver chloride equals	0.00007
	0.00006
	0.00137
	0.00150

Altogether we now have for the total weight of silver chloride:

[1] In this case the counterpoise contained no silver chloride, but in the most carefully conducted experiments the counterpoise contained as much of this salt as the test-crucible.

Weight of AgCl in crucible (vacuum)	13.65773
Asbestos, etc., washed through Gooch crucible	+0.00010
Dissolved	+0.00150
Loss on fusion	—0.00100
Corrected weight AgCl	13.65833

Ratio: AgCl : NaCl = 13.65833 : 5.56991 = 100.000 : 40.780

Mol. wt. NaCl (if Ag = 107.93 and Cl = 35.455) = 40.780 × 143.385 .. 58.473

Assumed atomic weight Cl 35.455

Hence atomic weight Na 23.018

Although most of the following determinations were essentially similar to this, a few small differences should be noted. In the twenty-seventh experiment the eight washings were extended over five days. In the sixty-fourth experiment, which must be considered as the best single experiment of all, the concentrations were lowered to tenth-normal, and twelve washings were made, the first within three hours, the last after a day's lapse. Considerable nitric acid was added to the first seven wash-waters. The slightly higher result of this experiment probably indicates diminished occlusion of sodium nitrate.

Three experiments were rejected, two because blackening of the silver chloride showed that the silver nitrate in the first wash-waters had not been eliminated by the subsequent washing with pure water, and one because of known loss of silver chloride. These oppositely erring results would have no effect on the final average if they had been included, but in such a table as this it seems advisable to include only results not vitiated by known sources of error. Below are given the final data and results of this comparison of silver and sodium chlorides.

THE RATIO OF SODIUM AND SILVER CHLORIDES (FINAL SERIES).

Expt.	Prep.	Wt. NaCl.	Wt. AgCl.	Parts NaCl equivalent to 100 parts AgCl.
13	K.	3.27527	8.03143	40.781
19	B.	5.56875	13.65609	40.779
20	A.	4.18052	10.25176	40.779
22	C.	4.54319	11.14095	40.779
23	D.	1.97447	4.84196	40.778
27	E.	3.97442	9.74547	40.782
61	H.	6.69495	16.41725	40.780
62	I.	2.88692	7.07955	40.778
63	J.	5.56991	13.65833	40.780
64	J.	5.85900	14.36693	40.781
		44.52740	**109.18972**	Aver. **40.780**

If the atomic weight of silver is taken as 107.930 and that of chlorine as 35.455, the atomic weight of sodium, calculated from the above average, will be 23.017, a result 0.14 per cent. lower than Stas's.

In spite of every effort to detect some error tending to diminish the atomic weight of sodium, and thus to cast doubt on this low value, and in spite of increasing precautions and increasing skill in the details of the experimentation, the last results are no higher than the very first one. Hence further prosecution of this method seemed to be of no avail. The reason for the difference between this value, 23.017 for the atomic weight of sodium and Stas's 23.048, is best discussed after the results of the comparison of sodium chloride with metallic silver have been detailed.

The Ratio of Sodium Chloride to Silver.

Since the time of Gay-Lussac the method of titration has been a avorite way of determining ratios between silver and soluble halogen salts. If the end-point were definite, this method would be capable of extreme accuracy. It involves no transference, collection or weighing of a precipitate; consequently, the introduction of silica or alkali from a glass-stoppered flask, occlusion of sodium nitrate, loss of asbestos fibers, and other sources of error are altogether avoided. After weighing the factors in the proper proportions, dissolving and precipitating, one has only to withdraw a portion of the mother-liquor and determine whether or not the true end-point of the reaction has been reached. It is not strange, therefore, that many eminent experimenters adopted this method in order to determine many atomic weights. The solubility of silver chloride, however, was a fact which Gay-Lussac, Pelouze, Dumas and many others, as well as Stas in his earlier experiments, did not consider; in consequence all used the wrong end-point. In his last experiments Stas, recognizing the solubility of silver chloride, attained the end-point in two ways. The first method consisted in titrating to the extreme limit with sodium chloride and then running back to the opposite extreme limit with silver nitrate; the true end point was assumed to be half way between the two limits.[1] The second method consisted in bringing the mother-liquor to such a point that two portions of it gave equal opalescent precipitates with silver nitrate and

[1] Oeuvres, **1**, 755. This is unsatisfactory for many reasons. See Richards: *Proc. Am. Acad.*, **29**, 82 (1893).

sodium chloride respectively; this was the end-point established by Mulder. Before accepting this latter method Stas attempted to prove for himself that a solution of silver chloride in water gave an equally intense opalescent effect with an excess of silver nitrate and sodium chloride. He concluded that the opalescence in the two cases was identical, but at the same time admitted that the opalescent precipitates were extremely unstable and varied continuously in appearance from the moment of precipitation to the time they had settled out completely.[1] At first, not hoping to improve essentially in this respect upon the methods of Stas we used this end-point and after few preliminary trials made eight careful determinations, using in all 33.1035 grams of pure salt and 61.0898 grams of pure silver. The atomic weight of sodium calculated for the average of these experiments was 23.032, with maximum and minimum of 23.040 and 23.023 respectively.

These experiments were of value as giving practice in the manipulation, but the extreme variation was so much greater than it ought to have been that clearly some undiscovered cause of variable error was present in the results.

A study of all the possible causes of irregularity eliminated all probabilities except the uncertainty of the end-point. The purity of the salt and the silver left nothing to be desired, for the same samples gave constant results when the silver chloride was weighed. Occlusion had been precluded by the use of solutions of not much over decinormal strength, and the mechanical operations were so extremely simple as to leave little opportunity for error.

Hence much time was spent in investigating the opalescent phenomena attending the precipitation of traces of silver chloride. The improved and precise nephelometer[2] served excellently in this tiresome research; we found that its readings could always be depended upon, and that if any irregularity occurred the fault was with the precipitate within the liquid and not in the means of observing this precipitate.

The first step in these tests was to prepare a solution of pure silver chloride, free from excess either of silver or of chlorine. For this purpose pure floccy silver chloride was very thoroughly washed in a flask by decantation. From time to time two nephe-

[1] Oeuvres, 1, 158.

[2] Richards and Wells: *Am. Chem. Jour.*, 31, 235 (1904).

lometer tubes were filled with the clear decanted wash-water; to one was added a milliliter of silver nitrate solution which contained a milligram of silver, and to the other a milliliter of an equivalent solution of sodium chloride. After stirring, these tubes were examined in the nephelometer within ten or fifteen minutes, and the intensities of the two opalescences were compared. No regularity could be detected in the results, successive trials varying over 50 per cent. from one another. For example, in one trial the tube containing an excess of silver was twice as intense in opalescence as the other, while in the following trial, with equal proportions of the same solution, it was only two-thirds as intense as the other. The average of a dozen comparisons confirmed approximately Stas's and Mulder's statement that silver chloride gives equal opalescence with the two precipitates, but the wide variation between the extremes emphasizes Stas's conclusions as to the uncertainty of the results.

Subsequent experiments showed that the presence of an electrolyte greatly accelerated the formation of the precipitate, indicating a colloidal transition stage. The preceding experiments had been almost free from electrolyte, and in view of this inference it is easy to see why the formation of the precipitate had been so irregular, for slight differences in the extent and speed of mixing might cause important differences in the coagulation of the colloid. Clearly, in making nephelometric experiments an excess of electrolyte must be present. Other possible causes of error, such as the effect of light and the presence of absorbed silver nitrate or common salt in the precipitated silver chloride from which the solution was made, were carefully guarded against in the further experiments. In order to avoid possible hydrolysis[1] nitric acid was always added.

Even when all these precautions had been taken, however, incomprehensible irregularities were still present in the results. It was then found that the *time* allowed for the formation of the opalescence had not been adequate, that in some cases one tube had clouded much faster than the other, but that in all cases neither tube had attained maximum intensity. It was found that as much time as eight hours was often needed to attain this maximum, but the time must not be too greatly extended, or some

[1] Mulder: "Die Silberprobirmethode" (1859), p. 72. Some of Mulder's observations in this direction may have been due to occluded material, but the danger of hydrolysis is not wholly to be despised.

or the precipitate will be deposited on the bottom of the tube. The performance of the precipitate when chloride is in excess is therefore not wholly parallel with that when silver is in excess, already described on p. 485.

In the course of these experiments several subordinate points were noted which are worth recording. When the opalescent precipitates were made directly in the tubes from sodium chloride and silver nitrate, having first one and then the other in excess, the speed of formation was not like that observed when a solution of silver chloride was treated with the two electrolytes. In the former case the maximum opalescence was attained more slowly and the tube containing an excess of chloride always became cloudy much more rapidly than that containing an excess of silver, while in the latter case the difference was much less marked. This adds to the evidence that the dissolved silver chloride is appreciably colloidal.

In view of these facts a new comparison was made. A quantity of silver chloride was precipitated in red light from cold decinormal solutions of silver nitrate and sodium chloride, washed twelve times with water weakly acidified with nitric acid and eight times further with pure water, the last washings being made in absolute darkness. Pure water containing such quantities of nitric acid and sodium nitrate as would occur in an actual mother-liquor, from a quantitative precipitation, was then added and the mixture allowed to stand with occasional agitations for a day. In making the nephelometer observations on the decanted liquid sufficient time was allowed for the precipitates to become constant. Three completely separate trials were made in the nephelometer, and of these are recorded below the lengths of liquids which seemed to be equally opalescent.

No. of observation.	Time.	Tube + $AgNO_3$.	Tube + NaCl.
65	After 8 hours	98 mm.	100 mm.
66	" " "	100 "	100 "
67	" " "	103 "	100 "
	Average	100.3 "	100 "

These observations, made with great care, settled every doubt about the correctness of the equal-opalescence end-point. Thus it is clear that Stas encountered difficulties with this method only because he, like all the previous experimenters, did not wait long enough to allow the opalescence really to establish itself in the absence of electrolyte to hasten precipitation.

The possible effect of light upon this end-point was another circumstance of interest, although not of immediate bearing on our quantitative work, since actinic light had been scrupulously excluded. In order to ascertain the effect of light the solution, already tested in observations 65, 66 and 67, was agitated in the flask for an hour at a distance of about a foot from a white incandescent electric light. Observations 68 and 69 were then made with the mother-liquor. It was then agitated in diffused daylight for another hour, an exposure which made the precipitate decidedly bluish, and observations 70 and 71 were taken.

Observation.	Tube + $AgNO_3$.	Tube + NaCl.
68	100 mm.	100 mm.
69	100 "	100 "
70	97 "	100 "
71	100 "	100 "
Average,	99 "	100 "

The solution thus gave the same results in the nephelometer as before. Böttger, in his study of the solubility by the conductivity method, also observed that the conductivity did not sensibly alter until the conductivity vessel was exposed to strong light for a considerable length of time. A slight coloring of the precipitate made no difference.[1] The explanation must be that chlorine thus set free does not ionize. According to Vogel[2] silver subchloride is insoluble in very dilute nitric acid. Hence neither an excess of ionized silver nor of chlorine should appear in the mother-liquor. Light, therefore, could not have heen the cause of any of the variations in the preceding observations, and its complete exclusion has been supererogatory.

Having thus, by many experiments, of which those given above are merely samples, assured ourselves that the true end-point may be decided by equality of opalescence when sufficient time is allowed to complete the opalescent precipitation, it became an important matter to make a conclusive series of analyses by this method.

In the first place a given piece of the purest silver was carefully weighed and was dissolved in a flask upon the steam-bath. For every gram of silver about 3 milliliters of nitric acid, of density about 1.20, were used. This density was secured by mixing

[1] "Löslichkeitsstudien," p. 32; *Ztschr. phys. Chem.*, **46**, 521 (1904).

[2] Gilbert's Annalen, **72**, 286.

pure distilled nitric acid of the usual concentration with an equal volume of water. After the silver was dissolved more water was added and the nitrous fumes were expelled by a brief very gentle ebullition. A tower of bulbs, ground to fit the neck of the flask, prevented any loss of silver nitrate during the operations as was proved by a special experiment. In this manner of treatment nitric acid always remained in slight excess.

Assuming a probable value for the atomic weight of sodium, the exact weight in air of salt equivalent to the weight of the given piece of silver was calculated and weighed out for fusion. There was always a slight loss of weight when the salt was fused in the platinum crucible, and if after fusion more than a milligram of salt was still required, approximately the required amount of well-dried salt was added at once by a platinum spatula. The amount so added never exceeded a few milligrams, and its introduction could have caused no error, since in our laboratory salt was not hygroscopic. The exact weight of salt, corrected to a vacuum, was obtained. Any further still slighter lack of equivalence was then made up by volumetric addition of the proper quantity of the same solutions which were to bring the mother-liquor to equal opalescences after the precipitation. Of course, the recorded weights include all these small additions.

Both salt and silver nitrate were diluted to a concentration about fifth-normal, and were then mixed in complete darkness with all possible precautions, the silver nitrate being very slowly poured into the salt solution. When in a day or two the precipitate had settled and the mother-liquor had become clear the latter was examined nephelometrically.

It was found convenient in determining the amount of a deficiency of either silver or chloride to calculate once for all the extent of this deficiency in terms of the ratio of lengths of the two nephelometer columns, giving equal apparent opalescence. This was in the first place, calculated by means of the law of concentration effect, but practically a slightly different value, based upon experience, was found to be more accurate. A ratio of 100 to 80 mm. was found to signify an excess or deficiency of 0.15 mg. of silver per liter, and other amounts in proportion. Since the average of many readings was probably accurate within 2 per cent., and the volume rarely exceeded a liter, it would appear that the end-point was determined within 0.02 mg. of silver. This does

not, of course, prove that the results are accurate to within this small margin, because other experimental details may have led to larger error. The difference between the maximum and minimum results corresponds, indeed, to a greater uncertainty, as will be seen. Hence the end-point is determined precisely enough for our purpose.

The final series of experiments, given below, includes only those experiments in which every known source of error was avoided. In order to illustrate the details of the method the full record of a single experiment, in so far as it does not repeat what has already been described, is here given.

EXPERIMENT 53.

	Grams.
Weight of sodium chloride (in vacuum) (Sample I).....	5.08685
Weight of silver (in vacuum) (Sample O)	9.38819

These were dissolved and mixed on February 2, 1904. After two days' agitation the mixture stood until next day, when an examination was made with the nephelometer. Two test-tubes were filled with the mother-liquor by means of a pipette, withdrawing 0.07 liter for this purpose. The two solutions were very nearly equal in opalescence. With occasional shaking the mixture was, therefore, allowed to stand yet another day in order to insure the thorough solution of possibly adsorbed material. The subsequent proceedings are summarized below:

FEBRUARY 4TH (0.07 LITER WITHDRAWN.)

Time of standing in nephelometer.	(*a*) Reading of tube with excess $AgNO_3$	(*b*) Reading of tube. with excess NaCl.	*a*/*b*.
30 minutes	45	54	0.83
2 hours	43	54	0.80
18 "	46	55	0.83

This reading indicates a slight deficiency of silver. Hence 0.15 mg. of silver in solution was added to the residual mother-liquor, and the mixture was occasionally shaken.

FEBRUARY 8TH (0.070 LITER WITHDRAWN).

Time.	*a*.	*b*.	*a*/*b*.
5 minutes	48	30	1.60
16 hours	60	57	1.05

There was now a slight *excess* of silver. Hence there was added 0.03 mg. of sodium chloride, corresponding to 0.06 mg. of silver.

FEBRUARY 16TH (0.07 LITER WITHDRAWN).

Time.	*a*.	*b*.	*a*/*b*.
15 minutes	50	39	1.28
1 hour	50	44	1.14
2 "	50	46	1.09
12 "	53	54	0.98
	36	35	1.03
	55	59	0.93
	33	33	1.00
	70	67	1.04
	52	53	0.98
	37	38	0.97
	24	23	1.04
Total,	360	362	1.00

Thus precise equality had been attained.

	cc.
Volume liquor now remaining	435
Withdrawn during trials	280
Original volume	715

If the first addition of silver had been made to the original total mother-liquor it would have been

$$0.15 \times \frac{715}{575} = 0.19 \text{ mg.}$$

Similarly,

$$0.06 \times \frac{715}{505} = 0.08 \text{ mg.}$$

Hence, extra silver required to produce equal opalescence in original mother-liquor = 0.19 — 0.08 mg. = 0.00011 gram.

Total silver = 9.38819 + 0.00011 = 9.38830 grams. This silver contained 0.0037 per cent. of impurity. The weight of pure silver present was 9.38795. Then Ag : NaCl = 9.38795 : 5.08685 = 100.000 : 54.185. Molecular weight NaCl = 107.930 × 54.183, if Ag = 107.930.

Molecular weight NaCl	58.482
Atomic weight Cl	35.455
Atomic weight of sodium	23.027

Ten such complete analyses are recorded in the table below.

THE RATIO OF SODIUM CHLORIDE TO SILVER.

Exp.	Preparations. NaCl.	Silver.	Weight salt (in vac.).	Observed weight silver (in vac.).	Correct weight of purest silver (in vac.).	Weight NaCl equivalent to 100.000 parts silver.
41.....	F	N	3.96051	7.30923	7.30896	54.187
44.....	K	N	2.32651	4.29371	4.29355	54.186
46.....	K	N	5.36802	9.90736	9.90699	54.184
45.....	G	M	4.00548	7.39237	7.39210	54.186
47.....	G	N	4.69304	8.66133	8.66101	54.186
52.....	H	P	3.27189	6.03864	6.03842	54.185
53.....	I	P	5.08685	9.38830	9.38795	54.185
55.....	J	P	3.66793	6.76977	6.76952	54.183
56.....	L	P	5.48890	10.13030	10.12993	54.185
57.....	L	P	3.55943	6.56933	6.56909	54.185
			41.42856		**76.45752**	**54.185**

The agreement of these results is now as good as could reasonably be expected. Whereas the earlier similar experiments, made before time enough had been allowed for the full development of the opalescence, showed an extreme variation in the results of 0.017; this extreme variation is now only 0.004. Since in these last experiments seven different specimens of salt were used, and three different specimens of silver, it seemed hardly probable that further work in the same direction would add certainty to the average. The chemical identity of the various preparations seems to have been proved.

The atomic weight of sodium calculated from the ratio 100.000: 54.185, the average of these ten determinations, is 23.027, if silver and chlorine are respectively assumed to be 107.930 and 35.455. This is 0.010 higher than the value obtained by reference to silver chloride—a difference which seems small in comparison with much quantitative chemical work, but which nevertheless is far greater than the sum of the probable experimental errors of the two series of results.

The conflicting outcome of all these carefully conducted experiments thus still remained not easily explicable. Their value for the atomic weight of sodium differed by over 0.1 per cent. from Stas's result, and furthermore, as has just been said, the comparison of sodium chloride with silver yielded a higher result, 23.027, than that found by comparison with silver chloride, 23.017. Both these discrepancies required explanation before the results could be accepted without reserve.

In the first place, much time was spent in the search for some possible error in our results. For example, several of our samples of salt, especially the preparation numbered K, were tested for lithium with the greatest care by fractional treatment with alcohol. The extreme mother-liquors showed no trace of the lighter metal, although in parallel experiments it was found that less than 0.01 per cent. of lithium chloride could be detected in this way, even by the simple flame test. This proportion could not affect the atomic weight of sodium by more than 0.002; but since no trace of lithium was found in any of the specimens of our salt tested, it is clear that our low value of the atomic weight could not be due to lithium. The constant results found with differently prepared samples from different sources seemed to exclude the possibility of the presence of the very few other metals which would yield too low a value for the atomic weight, namely, beryllium, magnesium, aluminum, and calcium. Acid could not have been present, since the material was usually prepared from salt finally crystallized from pure neutral solution, and was always fused in air. It gave, moreover, a wholly neutral reaction to methyl orange.

Because no flaw could be found in the operations leading to the new results, the conclusion was inevitable that the old ones were in error. In order to prove this beyond question, experiments were instituted in which each one in succession of the gravest faults already pointed out in Stas's work was imitated, in order to detect the individual errors introduced by each.

In the first place, two experiments were made in which the salt was prepared approximately according to Stas's method, the substance being fused with ammonium chlorplatinate. The salt thus prepared was compared with pure silver by means of the nephelometer, using, as Stas did, the opalescence which had been given only fifteen minutes to form. In this way 2.67137 and 5.51270 grams of salt needed, respectively, 4.92908 and 10.1717 grams of silver, corresponding to an atomic weight of sodium of 23.039 in each case. Since the value obtained from salt certainly free from platinum in the same way (p. 503) was 23.032, the difference of 0.007 may probably be ascribed to platinum, which had not been precipitated by thermal decomposition. Presumably, therefore, traces of platinum were present also in Stas's preparations.

In the next place, the effect of the occlusion of sodium chloride by silver chloride was quantitatively studied. It will be remembered that *Stas always dropped dry sodium chloride crystals into his silver nitrate solution* instead of adding the salt in the dissolved state. Such a procedure offered the maximum opportunity for the occlusion of sodium chloride. In the following experiments, made with the purest material (salt F and silver P) and executed with all the precautions outlined above, this error alone was purposely committed. After dropping in the solid salt, the mixture, after shaking two hours, was allowed to stand for a day, all according to the manner of Stas. In three experiments (Nos. 42, 51, 48,) 5.37853, 3.34018, and 5.29539 grams of salt required, respectively, 9.92510, 6.16392, and 9.77122 grams of silver, thus giving three determinations of the atomic weight of sodium, as follows: 23.033, 23.033, and 23.036, or, on the average, 23,034.

In the last experiment the gradual dissolving of this occluded salt was shown in an indubitable manner. On continued shaking throughout a week, more and more silver had to be added, until finally the mixture came to complete constancy at a point corresponding to 9.77264 grams of total silver. This quantity gives 23.028 as the atomic weight of the sodium, showing that within a week nearly, if not quite, all the occluded sodium chloride had been disengaged.

If, then, we sum up the effects which we have found for the three chief errors probably made by Stas in his *later* work, the following result is obtained:

Our value of the atomic weight of sodium from the ratio of sodium chloride to silver	23.027
Effect of too prompt reading of opalescence	+ 0.005
Presence of platinum in salt	+ 0.007
Occlusion of salt in silver chloride	+ 0.007
Result we should have obtained by Stas's complete method.	23.046

This result is so near that found by Stas's assistants in 1881 (23.050) as to make it seem probable that these errors really existed in Stas's work, and that the present investigation avoided them. The acknowledged presence of traces of gas in Stas's silver and silica in his salt may be neglected in this comparison as being errors of mutually opposing tendency and almost equal effect. The rectifying of previous work by means of a later correction is

always a doubtful process, and the above table is given only to show that Stas's small mistakes have all been traced.

It is not so easy to give the numerical magnitude of the correction to be applied to Stas's *earlier* work, which, as has been said, is inconsistent with the later work, because it gives the same result, although a wholly false end-point was used. It is probable, however, that in the early work, carried out by Stas himself, the precipitated silver chloride was much more thoroughly shaken with its mother-liquor than in the later work executed by MM. Nyst and Cabiliauw under Stas's direction. Continued shaking would diminish the solubility of the silver chloride, as well as disengage the occluded salt. Thus the decrease of the latter error might have balanced the effect of a greater error in the end-point, although this in its turn would be less marked than it would have been had the mixture been less thoroughly shaken.

All these considerations tend to support the present determination as against the verdict of the older ones, but no explanation is yet afforded as to the reason for the difference between the values 23.017 and 23.027 found by different processes in the present work. Long consideration of the matter led finally to the conclusion that the accepted value of the atomic weight of chlorine, 35.455, upon which the calculation depends, must be in error. Accordingly, this problem also was attacked experimentally. Before these lengthy experiments are recounted, brief mention must be made of the successful attack upon another doubtful point, which concerns the sodium chloride.

The Fusion of Sodium Chloride in Vacuum.

This matter has been given an especial heading because it is one which has never before received adequate treatment in an investigation of this kind. It is well known that many substances when fused in the air, dissolve either oxygen or nitrogen, or both, thereby increasing sensibly their weight. While it was hardly to be expected that this would be the case with sodium chloride, the point should not pass unchallenged in a research striving to attain the highest possible accuracy.

Hence two analyses were made of sodium chloride fused for some time in a platinum boat enclosed in a completely evacuated porcelain tube, and subsequently bottled in dry air in the often described "bottling apparatus." So far as we know these are the

only quantitative experiments ever made in which *all* the weighed substances were fused in a vacuum before weighing. It is true that Stas has shown that ammonium chloride sublimed in a vacuum gave the same equivalent referred to the silver as preparations sublimed in air, but this choice of ammonium chloride had the disadvantage that its two dissociation products possess different rates of diffusion, and moreover his silver had not been fused in a vacuum as ours had. The data and results are given below.

THE RATIO OF SODIUM CHLORIDE TO SILVER; BOTH SUBSTANCES FUSED IN A VACUUM.

No.	Sample salt.	Sample Ag.	Weight NaCl.	Weight purest corrected Ag.	Parts NaCl equivalent to 100 parts Ag.
59....	J	P	3.38684	6.25046	54.185
60....	J	P	4.68529	8.64634	54.188
				Average,	54.187

These experiments show that probably not enough gas is absorbed during fusion of the salt in air sensibly to alter the apparent combining weight. It is true that gases easily remain in supersaturated solution in liquid, and that long-continued relief from pressure is necessary to remove them, but fused sodium chloride is so mobile and possesses so low a density as to make the retention of much gas very unlikely. That air may be adsorbed by the cold salt is, of course, highly probable, but the surface of a fused lump is so small that the weight of this adsorbed air must be negligible. One would here expect a lower result from the salt fused in a vacuum, if gas were dissolved in the other experiments, but the results were in fact slightly higher, although not beyond the probable limit of experimental error. It appeared from tests with indicators that the salt remained strictly neutral after fusion in a vacuum, as it did in the air.

Being unable to conceive of any other sensible inaccuracies which could affect the analyses of the chloride of sodium, we turned our attention next to the composition of the chloride of silver, because of the before-mentioned suspicion that Stas was here also in error. An additional reason for this revision is found in the fact that the atomic weight of iodine, found at about the same time, has been found to be about 0.1 per cent. too low.[1]

[1] Ladenburg: *Ber. d. chem. Ges.*, **35**, 2275. Scott: *Proc. Chem. Soc.*, **18**, 112. Köthner and Aeuer: *Ber. d. chem. Ges.*, **37**, 2536 (1904). Also Leibig's *Ann.*, **337**, 123 (1904). Baxter: *Proc. Am. Acad.*, **40**, 419 (1904).

The Synthesis of Silver Chloride.

Many accurate analyses were made by Stas which involve, more or less directly, the atomic weight of chlorine, but of these we are concerned in the present paper only with those which compare silver with chlorine, because such alone could cause an error leading to the discrepancy under discussion. The experimental solution of the problem is thus a comparatively simple matter, to be accomplished by combining silver with chlorine. Among all Stas's experiments there seem to have been only seven which dealt directly with this ratio.[1] These were carried out by two methods. Of these methods one, the ignition of silver in a stream of chlorine, is acknowledged by Stas to possess errors, which he could not wholly correct. Hence, the three experiments made by this method are of doubtful value, and only four analyses remain for the purpose of obtaining directly this very important ratio. Even in these, the large, glass globes employed were more or less attacked by the strong acids or the fused chloride, and moreover Stas questioned the purity of the silver used in one case.[2] There is obviously no doubt of the need of obtaining more light upon this matter.

The fundamental requirements of a satisfactory synthesis of silver chloride are as follows: First, that the silver must be pure; secondly, that it must all be collected in the silver chloride, and thirdly, that this silver chloride must be pure. Because all the error accumulates upon the consequent atomic weight of chlorine, and is magnified in calculation, the requirements are usually rigorous.

The fulfilling of the first of these requirements has already been treated in detail, under the discussion of the preparation of silver. Our knowledge of the essentials of this easy but subtle process grew as the quantitative work on the systhesis of the chloride progressed. Whether in the future any one may be able to discover an unsuspected source of impurity in our purest silver, is of course impossible to say. At least, there can be no doubt that it was of distinctly a higher grade than the silver used by Stas, in most of his work.

In order to convert this silver wholly into the chloride without loss or illegitimate gain, two methods were used, for fear that in

[1] Stas: Untersuchungen (trans. Aronstein), 173, 175 (1867), Oeuvres, **1**, 333.
[2] Stas: (Aronstein), pp. 117, Oeuvres, **1**, p. 330.

one of these a constant error might lurk unsuspected. The first consisted in the usual method of solution in nitric acid and precipitation in dilute solutions, being essentially similar to that used in obtaining the ratio between common salt and silver chloride. The weighed silver was dissolved, with all the precautions used in previous work, and precipitated as chloride by hydrochloric acid, at concentrations of about fifth-normal. Hydrochloric acid was added in excess, and the precipitate was washed three times with dilute hydrochloric acid, in order to diminish as much as possible, the solubility of the silver salt. After collection on a Gooch crucible, drying at 150° and washing, the bulk of precipitate was fused in a porcelain or quartz crucible, and the loss in weight by fusion determined.

It would appear, at first, as if the result of this process could furnish nothing not directly calculable from a comparison of the two sodium series, in one of which common salt was compared with silver and in the other with silver chloride. This is not true, however, for in this previous work the precipitate formed in the presence of sodium nitrate and excess of silver nitrate, while in the present case an occluded alkaline salt could not be carried down, because none was present, and *all* the silver could be converted into chloride. For this reason the synthesis of silver chloride in the presence of nothing but volatile substances is an important step in the work.

As usual, in this case, also, improvement was effected as the work progressed, and here as before the less perfect tentative work is included in the preliminary table. The synthesis of silver chloride is a process of greater certainty than a metathetical reaction, for the reasons just stated, and hence finer corrections could be discovered and applied.

These corrections, in addition to the two already heeded, namely, that for the asbestos shreds carried away during filtration, and that for the enclosed wash-water set free on fusion of the chloride, were five in number.

The first of these was for the presence of a trace of silver chloride clinging to the collected asbestos shreds. This silver salt lost chlorine on ignition with the small piece of filter-paper used for collecting the shreds—a quantity which was determined by dissolving the residual silver and titrating with 1/100 normal sulphocyanate. The amount of chlorine thus lost on the average was 0.02 mg. in each synthesis—an amount which was added to the weight of the as-

bestos shreds. This correction might, in most cases, have been omitted, but it was determined for the sake of uncertainty.

The second of these corrections was for the slight solubility of silver chloride, even in dilute hydrochloric acid. This solubility may have been only apparent, the silver found being due to the imperfection of even the double filtration through asbestos and filter-paper—but in any case, it needed determination and correction. The average solubility, from five determinations (p. 486), was 1 part in 30,000,000 of water, which is about the order of the possible solubility of *undissociated* silver chloride, and hence may have represented that quantity. The determination was made by evaporating the hydrochloric acid solutions, rinsing out the dish with ammonia, and testing the resulting solution nephelometrically by comparison with similarly prepared known solutions of silver chloride, as has been said.

The third correction was for an occasional loss of chlorine by the silver chloride on fusion, owing either to the presence of silver nitrate or to traces of dust. The darkening thus caused represents a real, although often trivial, deficiency of weight, but, fortunately, this is easily restored by fusion in a mixture of pure chlorine and hydrochloric acid gas. Of course this process must not be adopted when silver nitrate is occluded during the analysis of a metallic chloride, for it would then lead to a large excess of silver chloride, but is perfectly safe in the present case. The only suspicion which attaches to it is the possibility that an *excess* of one of these gases might be dissolved. This is undoubtedly a real danger, unless the fused salt is exposed to the air and agitated in contact with it while fused. If this is done, we have assured ourselves by repeated experiments that no essential excess of chlorine remains dissolved.[1] Two facts pointed to this conclusion—first, that those samples of silver chloride, which after the preliminary fusion merely in air, were perfectly colorless, transparent, and pearly, gained no essential weight on fusion in chlorine (Expts. 80, R 2 R 3, final series page 524); and secondly that silver chloride fused in chlorine, properly freed from it, and subsequently again and again fused in pure air, lost no essential weight.

We always secured elimination of the possible trace of dissolved chlorine by continuing to fuse in air with occasional removal of the cover, and by carefully rolling the inclined crucible around,

[1] Dr. Baxter has come to the same conclusion: *Proc. Am. Acad.*, **40**, 432 (1904). And so also have Köthner and Aeuer, Lieb. *Ann.*, **337**, 127 (1904).

while held with forceps, during the solidification of the fused mass. Spreading the solid in this way makes it easier to fuse the salt once more without breaking the very fragile quartz crucibles.

The attacking of glass by chlorine in contact with silver chloride and a consequent loss of weight gave Stas considerable difficulty. Baxter has found that even porcelain is attacked in displacing iodine with chlorine in the silver salts. We did not greatly fear a loss of weight of the porcelain crucibles, since our chlorine was dilute, and was applied only for a few minutes; nevertheless, we adopted the use of quartz as an added precaution in the later experiments. No difference in results could be detected by its use.

A fourth correction which we sought to determine was for the possible volatility of the silver chloride during fusion. The constancy of weight on repeated fusion, already mentioned, seems to be sufficient proof for considering this correction as negligible. The conclusion is strengthened by the results of Biltz and Victor Meyer, who found silver chloride to be but slightly volatile at a much higher temperature.[1] It is not, of course, contended that silver chloride has no vapor tension at 500°, but only that the loss occasioned by its evaporation is too small to receive consideration.

During fusion, however, there is sometimes a slight spurting, or projection upward of minute drops of fused material. Hence the crucible must always be covered with an accurately weighed lid —a precaution which was always taken in the final experiments.

The phenomenon of spurting suggested that weighable quantities of air may be absorbed during fusion in air, and led to our effort to discover a fifth correction. Carefully conducted experiments showed, however, that there was no loss in weight of 3 grams of ordinarily fused silver chloride, when fused again in a vacuum. The fusions were conducted in a porcelain boat, covered with another inverted to serve as a lid. Slight traces of inclosed gas were noticed by Stas in many substances, but our quantitative experiments showed that they do not amount to a weighable quantity either in common salt or silver chloride. Thus, all the final experiments in this paper refer to substances fused *in vacuo*, and hence presumably as free as possible from inclosed air.

There were thus seven possible corrections, besides the correc-

[1] *Ber. d. chem. Ges.*, **22**, 727 (1889). Köthner and Aeuer found a volatilization of only 0.0002 gram in a case where several liters of gas had been passed over silver chloride during several hours. This agrees essentially with our result, for the likelihood of distillation in our case was much less (*loc. cit.*, p. 128).

tion of the weights to the vacuum standard, which might be applied to the results. Two of these, that for the possible volatility of silver chloride, and that for weight of dissolved air, were so small as to be entirely negligible. The chlorine lost from the traces of silver chloride clinging to the displaced asbestos shreds was added to the weight of these shreds, and is included therein in the tables below. The three other corrections are recorded in detail, in the following tables, which contain the original weight of the precipitate dried at 150°, as well as the final corrected values. The almost negligible correction for the solubility of silver chloride in dilute hydrochloric acid was computed, in the preliminary series, from the volume of the washings.

A few inessential changes in the mode of precipitation were occasionally introduced. In experiments 75, 76, and 79 both solutions were only about tenth-normal, and the number of washings was diminished; in R 1, the silver nitrate was very dilute, but the hydrochloric acid was somewhat concentrated.

As has been said, the tentative experiments were all classed together in a preliminary series, given immediately below. The table explains itself, for the most part, except perhaps the second column. This defines in the first place the designation of the silver, next the nature of the containing vessel on which it was fused, and last the atmosphere surrounding the metal during fusion. The word "blast" signifies that the sample thus qualified was fused in a blast-flame of illuminating gas and air, delivered from a clean nozzle, and that the resulting mass was cooled in the reducing flame.

Although not giving the true amount of chloride to be obtained from the purest silver, this table is highly instructive. It showed, in the first place, that even silver of this grade of purity must be 0.01 per cent. purer than that of Stas.[1] Again, it showed that

[1] There can be no doubt that this difference is due to the fact that Stas fused all the silver used in this part of his work in a porcelain crucible under borax and niter, thereby introducing both alkali and oxygen (Oeuvres, **1**, 328). His own subsequent experiments (Oeuvres **1**, 466) showed that this metal was at least 0.005 per cent less pure than his distilled granulated silver, which must, in its turn, have contained some oxygen. His still later elaborate search for oxygen in the silver is not satisfactory, because just before determining the oxygen in it he ignited it in a reducing flame, and because he sought to determine the oxygen only by heating to redness in a vacuum, a process which may have set free only the superficial oxygen. Dumas found 0.008 per cent of oxygen in similar silver by fusion *in vacuo* (*Ann. chim. phys.*, **14**, 289 (1878)), and Mallet found that silver fused like Stas's purest in the oxyhydrogen blast contained 0.005 per cent of oxygen (Phil. Trans., **171**, 1020 (1880)).

SYNTHESIS OF SILVER CHLORIDE (PRELIMINARY SERIES.)

No. of exp.	Description of silver sample; support; and environment during fusion.	Observed weight of silver (vac.). Grams.	First approximate weight AgCl (vac.). Grams.	Corrections to AgCl. Asbestos residue (add.). Mg.	Loss on fusion (subtr.). Mg.	Gain in Cl (add.). Mg.	Correct. for solubility (add.). Mg.	Correct weight AgCl (vac.). Grams.	Parts of AgCl produced from 100,000 parts Ag. Per cent.
65	P, lime, vacuum	9.06483	12.04416	0.10	0.79	0.12	0.06	12.04865	132.861
66		8.39217	11.14987	0.35	0.57	0.14	0.06	11.14985	132.860
70		5.37429	7.14072	0.26	0.51	0.03	0.06	7.14056	132.865
								Average,	132.862
67	P, carbon, blast	8.08222	10.73844	0.46	0.49	0.22	0.06	10.73869	132.868
68		7.08517	9.41382	0.20	0.50	0.04	0.06	9.41362	132.864
71		7.97715	10.59854	0.45	0.82	0.14	0.06	10.59837	132.859
								Average,	132.864
72	S, lime, vacuum	8.11978	10.78751	0.36	0.38	0.09	0.09	10.78767	132.857
73		8.53452	11.33904	0.28	0.40	0.09	0.06	11.33907	132.861
74		6.73284	8.94497	0.42	0.51	0.14	0.09	8.94511	132.858
75		8.91366	11.84225	0.48	0.48	0.09	0.06	11.84240	132.857
76		9.72295	12.91736	0.56	0.41	0.09	0.09	12.91769	132.858
								Average,	132.858
79	U, carbon, H_2	8.63961	11.47877	0.30	0.61	0.07	0.09	11.47862	132.860
R 1	V, lime, blast	11.13795	14.79856	0.24	0.50	0.10	0.09	14.79849	132.865
								Total average,	132.861
								Stas found,	132.848

at least a part of the difference between the two new values for the atomic weight of sodium is due to an error in the assumed atomic weight of chlorine used in the calculations. It proved that the analytical method was capable of yielding very constant results with a given sample of silver (Expts. 72 to 76). It confirmed previous results[1] in showing that portions fused in these various ways were not very different, but showed slight variations according to the method of fusion employed. It furnished a means of determining, by later comparison of one or the other of these results with those from the purest silver, the exact grade of purity of the various specimens of silver used in the previous work in this laboratory, in particular that used in the earlier part of the present research. Finally, it furnished sufficient clue to the precautions which must be taken to secure yet purer silver.

A careful study of this table led to the conclusion that a reducing environment is necessary to eliminate traces of oxygen during fusion, and that lime is better than carbon as a support during fusion. The details of this matter have already been described under the heading "Preparation of Materials" (page 476), and need not be further detailed here. Suffice it to say that the silver used in the experiments recorded in the table (on p. 524) was free from the sources of error thus detected.

The final series comprehends ten experiments, made with four samples of silver prepared entirely independently by three different experimenters (Dr. Baxter having very kindly given us a piece of his purest silver used in the determination of the atomic weight of iodine, and each of the authors having made separate samples) and two entirely different methods of synthesis.

Of these methods of synthesis one has already been described, namely, the usual method of solution of the silver in nitric acid, precipitation by hydrochloric acid, and filtration on a Gooch perforated crucible. Of course all the precautions and corrections already discussed were applied with as much care as possible. All the vessels used were afterwards washed with a little ammonia, and the washings tested nephelometrically in order to be sure that no silver was lost by adsorption on the vessels. By this method Expts. 69, 77, 78, 80, 81, R 2 and R 3 were made. Further unvaried repetition of this process seemed to promise no further light on the question.

[1] Richards: *Proc Am. Acad.*, **29**, 65 (1893).

Although this method seemed to leave little or nothing to be desired as regards accuracy, it was nevertheless deemed advisable to test it by making a few syntheses by means of an entirely different process, in which all the vessels coming in contact with the precipitate could be weighed. Accordingly a new method was devised, a modification of one of those used by Stas, employing quartz vessels instead of glass. A quartz dish was accurately weighed by substitution of a counterpoise of a similar composition, surface area, and weight. A watch-glass to serve as its cover was weighed in a similar fashion separately. A weighed piece of silver was placed in the dish, which was supported in a large empty "desiccator," whose bottom and sides were well moistened with pure water. The silver was covered with redistilled nitric acid of the usual strength and left covered both by watch-glass and desiccator lid to dissolve slowly over night in a warm place. On the next day the moisture on the glass cover was washed with great care to avoid the slightest spattering into the quartz dish. If any spattering occurred it was caught in the large desiccator, which, having been tightly covered, served also to catch all spray proceeding from the solution of the silver. In two experiments the silver recovered from the water in the desiccator amounted to only 0.02 mg. when estimated by the nephelometer, and in one no silver at all was found in the desiccator.

Hydrochloric acid gas was next allowed to play upon the surface of the silver nitrate solution in the quartz dish, and the resulting chloride was caused to sink to the bottom by means of a very small glass stirrer, afterwards carefully rinsed. The remaining solution of nitric and hydrochloric acids was then evaporated to dryness upon a clean steam-bath under an appropriate hooded cover (Victor Meyer funnel). The atmosphere around was kept as pure as possible during this evaporation, which was usually conducted during the night. Finally the silver chloride was fused in the quartz dish, supported inside of a large porcelain crucible, from which the products of combustion of the gas-flame were suitably deflected. The weighed cover caught the one or two minute drops projected upwards during the act of fusion. Then a mixture of chlorine and hydrochloric acid gas was passed in, so as to convert any residual traces of nitrate of silver wholly into silver chloride. The precaution of cooling, mentioned on page 517, enabled us to preserve the quartz dish intact through the

analyses, notwithstanding the extreme fragility of thin fused quartz. Its weight was conserved through three experiments within the limits of the accuracy of the weighing. Expts. 83, 84 and 85 were made by this method. One of these (Expt. 84) is given below in detail.

Corrected weight of silver in air	6.25336
Vacuum correction	0.00018
Weight of silver in vacuum	6.25318
Excess weight quartz dish over counterpoise	0.21510
Excess weight dish and fused AgCl over counterpoise	8.52279
Weight of silver chloride in air	8.30769
Excess weight cover glass over counterpoise	0.09972
Excess weight cover and spattering over counterpoise	0.09974
AgCl projected and caught on cover-glass	0.00002
AgCl found in desiccator by nephelometer	0.00002
Vacuum correction	0.00061
Total weight of silver chloride in vacuum	8.30834

$$Ag : AgCl = 6.25318 : 8.30834 = 100.000 : 132.866.$$

This second method, which avoids any transference of material whatever, is an unusually searching check upon the method employing the Gooch filter; and the fact that the two methods confirm each other to the limit of weighing is a most satisfactory criterion of each, supporting the previous similar work with sodium chloride as well.

The following table is complete, including all the experiments made with the purest material, and every precaution. The experimental work, as well as the preparation work, was the product of more than one experimenter, the senior author having made, from beginning to end, the syntheses numbered R 2 and R 3 (as well as R 1 in the preliminary series)[1], and the junior author having made all the others. The two experimenters used differ-

[1] The hydrochloric acid used in these experiments was three times successively treated with small amounts of permanganate and boiled to eliminate bromide, and each time distilled.

SYNTHESIS OF SILVER CHLORIDE (FINAL SERIES).

Exp.	Description of silver.	Observed weight Ag (vac.). Grams.	First approximate weight AgCl (vac.). Grams.	Corrections to AgCl. Abestos residue. (Add.) Mg.	Loss on fusion. (Subtr.) Mg.	Gain in Cl_2. (Add.) Mg.	Corrected for solubility. (Add.) Mg.	Corrected weight AgCl (in vac.). Grams.	Parts AgCl produced by 100,000 parts Ag. Per cent.
69	Baxters lime, H_2.	7.24427	9.62517	0.16	0.40	0.09	0.06	9.62508	132.865
77	T, lime, H_2	8.30502	11.03312	1.10	0.14	0.67	0.09	11.03484	132.870
78		7.29058	9.68547	1.23	0.12	0.09	0.09	9.68676	132.867
80		8.58472	11.40578	0.57	0.32	0.02	0.09	11.40614	132.866
81		8.01318	10.64632	0.34	0.32	0.05	0.09	10.64648	132.862
R 2		9.77160	12.98283	0.74	0.37	0.02	0.13	12.98335	132.868
83		7.98170	10.60528	....	....	....	....	10.60528	132.870
							Average 7 experiments,		132.867
R 3	V, lime, vacuum	11.49983	15.27978	0.44	0.66	0.03	0.05	15.27964	132.868
84	W, lime, H_2, vac.	6.25318	8.30834	....	....	....	....	8.30834	132.866
85		7.72479	10.26360	....	....	....	....	10.26360	132.866
							Average 3 experiments,		132.867
	Total	**82.66887**	.....	....	....	....	....	**109.83951**	132.867
							Final average,		**132.867**

ent balances, different weights separately standardized, and different preparations throughout, in order to secure additional certainty.

This result, namely, 132.867 parts of the chloride from 100.000 of silver has a "probable error," computed according to the method of least squares of about 0.0005. This so-called probable error, of course, gives no clue as to possible constant errors involved. A better idea of the chemical trustworthiness of the result is obtained by comparing the data furnished by the two different methods of synthesis. The averages of the seven determinations by the method of filtration is 132.8666, while that of the three by the method which involves no transference of material (83, 84, 85) is 132.8673. These are both within the range from the mean 132.8668 indicated by the "probable errors" of the respective averages, and hence may be considered as identical.

If the comparison be made according to the environment of the silver during fusion, a similar result is obtained. The silver fused in hydrogen gives an average of 132.8667, while that fused in a vacuum gives 132.8668. Again, this is essential identity.

In view of these facts, the fact that all probable errors tend to lower the result, and the multitude of precautions which eliminated errors from these figures, it is not unsafe to conclude that 100.000 parts of the purest silver really yields as much as 132.867 parts of silver chloride. This conclusion confirms the comparison of the silver and silver chloride indicated by the work on sodium, and shows that no great occlusion of sodium nitrate could have taken place there. It furnishes, moreover, a means of determining by comparison the purity of any other specimen which has been used in the quantitative synthesis of silver chloride by either of the foregoing methods. For example, it shows that the silver used in the work on sodium—silver which yielded 132.862[1] parts of chloride—must have contained $5/132867 = 1/27000 = 0.0037$ per cent. of impurity.

The New Atomic Weights of Sodium and Chlorine and Their Effect on Other Atomic Weights.

From the preceding description of the syntheses of silver chlo-

[1] See Syntheses 65, 66, and 70 given in the table on page 520. The silver used in these syntheses was exactly similar to some of that used in the work on sodium. In the same way, if Stas's method of synthesis is considered as comparable with ours, his silver must have contained $(132867 - 132848) : 132867 = 0.014$ per cent of impurity. It is doubtful, however, if the methods of synthesis are strictly comparable.

ride it is clear that 100,000 grams of the purest metal yields 132.867 grams of chloride. If then the atomic weight of silver is taken as 107.920[1] (a convenient value to assume for preliminary calculation) the molecular weight of silver chloride becomes by simple proportion 143.390, and by difference the atomic weight of chlorine becomes 35.470.[2] This value is about 0.05 per cent. greater than the value announced by Stas; and the change produces a serious effect on a number of atomic weights. It is, of course, impossible to be perfectly certain of the accuracy of the new value, because it may contain concealed within it some entirely unsuspected source of error, but at least it is free from the real mistakes in the earlier work. It was reasonably certain that at least ten more syntheses would be needed to affect the value one unit in the third decimal place, if the further results varied no more widely than those recorded above in the final series. Hence it seems unlikely that chlorine is above 35.471 or below 35.469, if silver is taken as 107.920.

What, now, is the effect of this new value upon the atomic weight of sodium? In the table given upon page 501 it is shown that 100,000 grams of silver chloride could be obtained from 40.780 grams of sodium chloride. If now silver chloride is taken as 143.390, sodium chloride becomes 58.474, and by subtracting the new value for chlorine, 23.004 is obtained as the new value for sodium.

This is not, however, the only value for sodium which may be calculated from our results. On page 510 has been given a table showing the results of ten experiments on the comparison of sodium chloride with silver direct and on page 514 the results of two more. These determinations were made before we had discovered the best method of obtaining pure silver; but the trace of impurity is allowed for in those tables, and it is safe to conclude that 100,000 parts of the purest silver are equivalent to 54.185 parts of sodium chloride. If, then, silver is taken as 107.920 and chlorine as 35.470, sodium becomes 23.007.

[1] F. W. Clarke has for a long time accepted this value, and it now assumed because it is probably nearer the true value than 107.93.

[2] In this connection it should be pointed out that Leduc called attention to the fact that if Stas's silver really contained as much oxygen as Dumas said it must, chlorine would become 35.47. *Compt. Rend.*, 1901. The somewhat lower value, 35,467, first announced, informally, as the result of the present work was calculated from some of the slightly erroneous preliminary experiments recorded on p. 520 of the present paper.

Thus two entirely independent values, calculated from two entirely separate series of experiments, yield respectively the values 23.004 and 23.007 for the atomic weight of sodium. Of these two the latter is somewhat the more trustworthy, because, as has been said, the occlusion of sodium nitrate by the precipitate does not affect it; hence the mean may be taken as 23.006. This value is probably not more in error than two units in the third decimal place, if silver is 107.920, although of course the same remark applies to it that was made concerning the possible error of the value for chlorine. If silver is taken as 107.930, sodium becomes 23.008, and chlorine 35.473.

The new values are then as follows:

	(Ag = 107.920.)	(Ag = 107.930.)
Atomic weight of sodium	**23.006**	**23.008**
Atomic weight of chlorine	**35.470**	**35.473**

The new value for sodium is nearly 0.2 per cent. less than that found by Stas—a percentage error much greater even than that made by him in the case of iodine. It will be noted that the likely error of the new result is only about a twentieth of the difference between the new result and that of Stas. Some will attach significance to the fact that both the new values bring the elements nearer to the demands of Prout's hypothesis.

These new values affect greatly the figures in the second decimal place of all other atomic weights depending directly or indirectly upon chlorine, sodium or silver. The number of elements thus affected is so great and the relations so complicated as to render imperative a recalculation of all atomic weights. Nitrogen, as computed from ammonium chloride, will be especially affected, the new value approaching more nearly that required by Avogadro's rule than the old. Probably, however, it will be best to delay this systematic recalculation until a few other new data shall have been obtained—in particular new analyses of potassium chloride, silver chlorate, the bromides, the sulphides and similar important compounds. Some of these are already under way at Harvard, and others will be undertaken at once.

In conclusion, it is a pleasure to acknowledge our great indebtedness to the Carnegie Institution of Washington, without whose liberal support the present investigation could not have attained its present thoroughness or precision.

Summary.

The investigation consisted of a very careful quantitative study of three ratios, namely, AgCl : NaCl, Ag : NaCl and Ag : AgCl. The effort was made to test every operation involved in the execution of the experiments. In the course of the work the following points were developed:

(1) Sodium chloride, obtained from many sources and purified in many ways, always gave the same equivalent weight.

(2) Fusion in vacuum of salt already fused in air caused no change in this equivalent weight.

(3) Silver chloride precipitated from aqueous solutions always occludes traces of other substances present, and those traces can not always be eliminated. Very dilute solutions must hence be used in precipitation.

(4) The conditions governing the occlusion and release of these impurities were minutely studied, and it was shown that Stas's method of dropping solid salt into a silver solution causes occlusion of salt. Many considerations important in all precise chemical work are discussed.

(5) A careful study of the solubility of silver chloride was made, and the precautions necessary in using the nephelometer in the estimation of traces of chloride and silver were ascertained.

(6) Fused silver chloride probably contains traces of dissolved air, but not enough to affect essentially its weight, since subsequent fusion in vacuum caused no appreciable loss of weight.

(7) The most difficult question in the purification of silver was found to be the elimination of the inclosed mother-liquor without introducing other impurities. Fusion on pure lime, first in pure hydrogen and then in a vacuum, is the safest method. Stas's silver must have contained at least as much oxygen as Dumas claimed.

(8) In ten experiments 44.5274 grams of sodium chloride yielded 109.1897 grams of silver chloride.

(9) In twelve other experiments, entirely distinct from these, 49.5007 grams of sodium chloride were found to be equivalent to 91.3543 grams of the purest silver.

(10) In ten other experiments, again entirely distinct from the preceding, 82.6689 grams of the purest silver yielded 109.8395 grams of silver chloride. Two very different methods of synthesis

were used in this series, and the silver came from various sources, these variations being without effect on the result.

(11) If the atomic weight of silver is assumed to be 107.920, sodium is found from the above results to have an atomic weight of 23.006 and chlorine an atomic weight of 35.470.

(12) Many other atomic weights are affected, in their second decimal places, by these changes. In particular, certain slight anomalies previously noticed in Harvard work are explained by them, and the atomic weight of nitrogen computed from ammonia is brought nearer to the value required by Avogadro's rule. Other anomalies appear in other places, however, and it is clear that many new atomic-weight investigations must be instituted to explain them, with due attention to hitherto unheeded dangers, especially of occlusion.

CALCIUM SULPHATE IN AMMONIUM SULPHATE SOLUTION[1].

By Eugene C. Sullivan.

Received February 10, 1905.

Arrhenius[2] rejects the idea of constant concentration of the non-dissociated portion of a salt in its saturated solution on the following grounds:

In a saturated water solution of thallous chloride (TlCl) the non-dissociated salt, calculated from the electric conductivity, is 0.00179 normal, while in the presence of 0.8 normal potassium chloride the total solubility of thallous chloride is only 0.00170 normal,[3] *i. e.*, less than non-dissociated thallous chloride alone in pure water solution; of this 0.00170 perhaps 40 per cent. is dissociated, leaving the non-dissociated portion apparently in decidedly lower concentration than in the water solution. There are other similar cases.

Further, Arrhenius demonstrates that the isohydric principle applied to the calculation of conductivity of mixtures gives satisfactory results: Solutions having the same ion in equal concentration afford a mixture whose conductivity is a mean of the individual conductivities; that is, the dissociation in the case of iso-

[1] Published by permission of the Director of the United States Geological Survey.

[2] *Ztschr. phys. Chem.*, **31**, 221 (1899).

[3] A. A. Noyes: *Ztschr. phys. Chem.*, **9**, 613 (1892).

hydric solutions is not affected by mixing. This is extended to any mixture of electrolytes having a common ion by imagining the mixture formed by bringing together isohydric solutions of such electrolytes. MacGregor[1] has formulated a graphic method of thus getting at the conductivity of mixtures, and the results agree excellently with those obtained by actual measurement. The point being thus established that the composition of the mixture, so far as it may be judged at all by the conductivity, is ascertainable by application of the isohydric method, Arrhenius calculates by this means the relative amounts of dissociated and non-dissociated silver salt present in the case of sodium salts of certain organic acids saturated with the corresponding silver salts.[2] The solubilities of the silver salts in the solutions were determined by experiment, but no attempt was made to measure conductivity. The concentration of the non-dissociated silver salt in the saturated solution as thus calculated is not constant.

The measurements presented in the following paper, made originally for a somewhat different purpose, are found to show that the isohydric principle applied to ammonium sulphate solutions saturated with calcium sulphate gives results for the conductivity of the mixtures agreeing with those actually observed, and varying somewhat from those which might be expected if the concentration of non-dissociated calcium sulphate were the same throughout all the solutions.

The calcium sulphate used was in the form of perfectly clear transparent plates of gypsum, $CaSO_4.2H_2O$ (selenite). The only impurity detected was a faint trace of chloride. The ammonium sulphate, purified by repeated crystallization, contained a slight non-volatile residue (1.2 mg. in 10 grams) for which the corresponding correction was applied to the weight of calcium sulphate found.

The gypsum was coarsely broken, washed several times by decantation with the solvent, and slowly revolved (three revolutions per minute) in a thermostat at 25° C. The flasks used were of Jena glass, steamed, closed with rubber stoppers and sealed with paraffin. The solution after saturation was, without removal from the thermostat, filtered upward by suction through a very small paper filter into a second flask, also in the thermostat. For analysis a weighed quantity of the solution was evaporated

[1] *Trans. Nova Scotian Institute of Science*, **9**, 101 (1895).
[2] *Ztschr. phys. Chem.*, **31**, 224 (1899).

in platinum, the ammonium sulphate very slowly and carefully driven off by heat, the dish containing calcium sulphate heated to redness and weighed.[1] Known quantities of gypsum treated with sulphuric acid, which was then expelled by heat, gave results agreeing closely with those calculated. They ran pretty uniformly 0.1 per cent., rarely 0.2 per cent. higher than calculated. Known quantities of gypsum, mixed with ammonium sulphate and recovered in the same manner as in the case of the saturated solutions analyzed, gave somewhat greater variations, due to mechanical loss on driving off the ammonium salt, and also to retention of the latter even at high temperatures. The mean of duplicates worked in this way was usually, however, but 0.1 to 0.2 per cent. higher than the expected result.

For gypsum dissolving in water alone equilibrium was reached from either direction. Supersaturation was obtained by revolving one and a half hours at 35° to 40° and cooling to 25°. After standing over night at 25° the specific conductivity at that temperature in two solutions was 0.002225 and 0.002227 respectively, indicating a concentration over 0.5 per cent. higher than that of the saturated solution. On revolving further, the conductivity became 0.002212 and 0.002215 respectively, identical with the result found by revolving at 25° continuously.

The solubilities are shown in Table I. Weighings are reduced to vacuum. Specific gravities are accurate to two or three units in the fifth decimal. Concentrations are in mols per liter.

The calculated solubilities were derived by a series of approximations from the mass-law equations, k being furnished by the conductivity of the salt in the concentration involved; any dissociation of ammonium sulphate other than into $2NH_4^{\cdot}$ and $SO_4^{''}$ is disregarded.[2] Symbols in brackets indicate concentrations:

[1] Anhydrous calcium sulphate obtained in this way or by addition of concentrated sulphuric acid and evaporation is not hygroscopic and may be exposed to the air indefinitely without change in weight, although the anhydrous salt which results from heating gypsum sufficiently to expel all water without loss of sulphur trioxide is, as is well known, hygroscopic. Furthermore, the anhydrous salt obtained by treatment with concentrated sulphuric acid gives off sulphur trioxide on heating less readily than does gypsum. This behavior is suggestive of a more intimate union with the water than is expressed by the formula $CaSO_4\ 2H_2O$. Compare the results obtained by Gooch and McClenahan, *Ztschr. anorg. Chem.*, **40**, 24 (1904), with metallic chlorides containing "water of crystallization."

[2] A. A. Noyes (*Phys. Rev.* **12**, 31 (1901) and *Ztschr. phys. Chem.*, **36**, 63 (1901)), concludes from the constancy of the transference number with varying concentration that in 0.1 molal potassium sulphate solution the concentration of KSO_4' ions, if they are present at all, does not exceed a very few percent of the total concentration. Kümmell (*Ztschr. Elektrochem.*, **9**, 975 (1903)) reaches a similar conclusion, on other grounds, with regard to magnesium chloride.

TABLE I.—SOLUBILITY OF CALCIUM SULPHATE IN AMMONIUM SULPHATE SOLUTIONS.

Concentration $(NH_4)_2SO_4$.	Mixture revolved, hours.	Grams $CaSO_4$ per 100 cc. found.	Means.	Concentration $CaSO_4$. Found.	Concentration $CaSO_4$. Calculated.	Weight in grams of 1 cc. 25° C. Solvent.	Weight in grams of 1 cc. 25° C. Solution saturated with gypsum.
0.00	3	0.2085	0.2083	0.01530		0.99707	0.99911
	6½	0.2084					
	7	0.2081					
0.0009766	I 6	0.2038	0.2043	0.01500	0.0150	0.99711	0.99911
	II 16	0.2047					
0.001953	I 4½	0.1989	0.1996	0.01466	0.0146	0.99721	0.99920
	II 16½	0.2004					
0.007812	I 6	0.1802	0.1807	0.01327	0.0129	0.99765	0.99946
	II 16	0.1812					
0.01563	I 3½	0.1651	0.1658	0.01218	0.0113	0.99832	0.99995
	II 12	0.1664					
0.03125	I 19	0.1536	0.1540	0.01131	0.0099	0.99953	1.00104
	II 19	0.1544					
0.06250	I 3	0.1440	0.1440	0.01058	0.0088	1.00201	1.00341
	II 15	0.1440					
0.1250	I 6	0.1453	0.1455	0.01069	0.0081	1.00681	1.00817
	II 17	0.1456					
0.2500	I 3	0.1617	0.1617	0.01187	0.0078	1.01606	1.01763
	II 8	.....					
0.7500	I 5	0.2328	0.2330	0.01712		1.05143	1.05344
	II 10	0.2331					
1.500	I 4½	0.3299	0.3330	0.02446		1.10059	1.10324
	II 8½	0.3360					
3.000	I 4	0.4476	0.4500	0.03305		1.18843	1.19149
	II 8	0.4523					

$$[Ca^{\cdot\cdot}][SO_4''] = k_1[CaSO_4].$$

$$[NH_4^{\cdot}]^2[SO_4''] = k_2[(NH_4)_2SO_4]$$

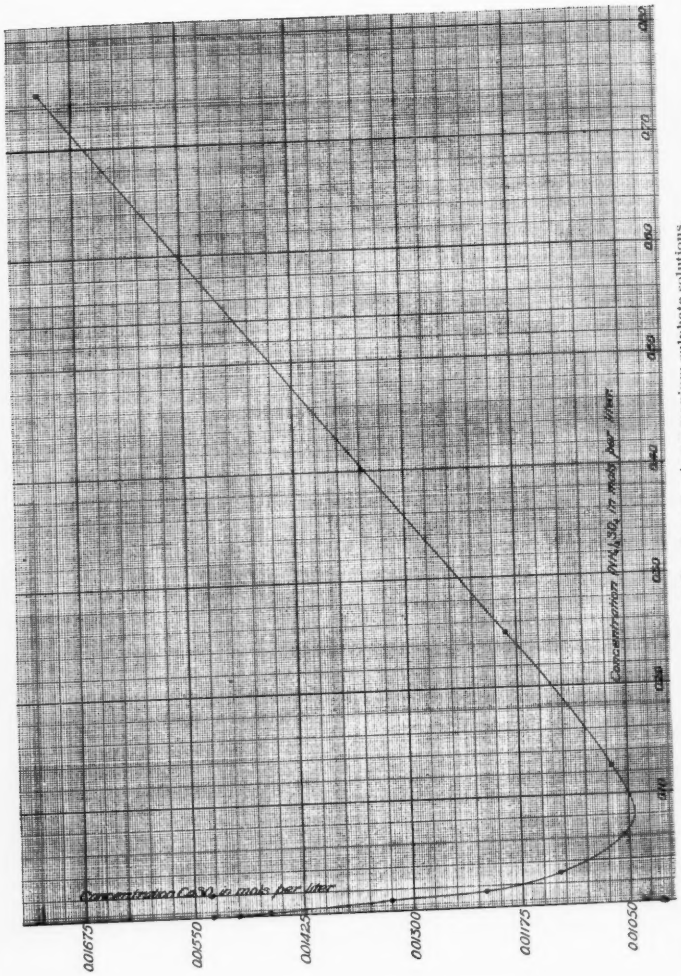
The results calculated agree well with observation in the two most dilute solutions. From there on the solubility found is greater than calculated even in those dilutions in which the conductivity indicates absence of double salt.

Plotting the observed results and passing a curve through the points (Fig. 1) one notes a sharp decrease in solubility of gypsum with the first addition of ammonium sulphate. As the concentration of the latter increases (to about 0.02) the fall becomes more gradual, and the solubility passes through a minimum with about two-thirds of its original value when the concentration of ammonium sulphate is about 0.09 molal. From this point the solubility gradually rises, reaching the same value as in water for an ammonium sulphate concentration of about 0.6 molal; with 3 mols ammonium sulphate per liter over twice as much gypsum dissolves as in water. The curve is similar in form to that found by Cameron and Seidell[1] for calcium sulphate in sodium sulphate solution.

MacGregor[2] applies Arrhenius' principle of isohydric solutions to the calculation of the conductivity of mixtures, finding by a graphic method what isohydric solutions when brought together afford a mixture identical in composition with that under examination. The mixture is conceived as containing each electrolyte segregated in a definite portion of the volume of the solution, the solutions in these partial volumes being isohydric and their conductivity therefore not changed by mixing, *i. e.*, the conductivity of the mixture is the mean of the conductivities of the components. With given quantities of salts and a given total volume to which they may be dissolved there is, in general, only one proportion in which the solvent may be divided between the salts to form isohydric solutions. By plotting the ion concentration as a function of the volume for the given quantity of each salt it may be found by inspection of the curves in what volumes the given quantities of salts must be dissolved in order that the solutions shall contain the common ion in identical concentration and that the sum of the volumes shall equal the volume of the mixture.

For example:

[1] *J. Phys. Chem.*, **5**, 643 (1901); Cameron and Breazeale: *J. Phys. Chem.*, **8**, 335 (1904).
[2] *Loc. cit.*



Solubility of gypsum in ammonium sulphate solutions.

1/1024 molal $(NH_4)_2SO_4$ (concentration = 0.0009766) dissolves gypsum in such quantity as to form 1/66.66 molal $CaSO_4$. To simplify calculation consider that quantity of this solution which contains one mol $CaSO_4$; we have then 66.66 liters of a mixture containing 33.33/512 mol $(NH_4)_2SO_4$ and one mol $CaSO_4$. What parts of this volume must be assigned respectively to these quantities of salts in order that the resulting solutions shall be isohydric?

Inspecting the curves (for $CaSO_4$ ion-concentration as function of the volume in which one mol is dissolved, for $(NH_4)_2SO_4$ ion-concentration as function of the volume in which 33.33/512 mol is dissolved), we find

1 mol $CaSO_4$ dissolved in 60.38 liters (spec. cond. 0.002346) and
33.33/512 mol $(NH_4)_2SO_4$ " " 6.28 " (" " 0.0002635)

Sum 66.66 "

contain the ion SO_4'' in like concentration (0.00848) and the sum of the volumes is identical with the volume of the original mixture.

On mixing such solutions each leaves the conductivity of the other undisturbed and the conductivity of the mixture is the sum of the specific conductivities multiplied by their respective volumes, the whole divided by the total volume:

$$0.002346 \times 60.38 = 0.1417$$
$$0.0002635 \times 6.28 = 0.0166$$

$$0.1583 \div 66.66 = 0.002375,$$

the calculated specific conductivity of the mixture.

The method in the hands of MacGregor and his associates[1] permits of the calculation of the conductivity of dilute mixtures—up to a concentration of about 0.25 mol per liter—with a mean deviation from the observed result at worst scarcely greater than the limit of error of an observation, which is estimated as 0.25 per cent. Na_2SO_4–K_2SO_4, K_2SO_4–$CuSO_4$, $ZnSO_4$–$CuSO_4$, NaCl–$BaCl_2$, K_2SO_4–$MgSO_4$ were among the mixtures examined.

Table II gives the results of the conductivity measurements for ammonium sulphate solutions saturated with gypsum. These were made, except in the concentrated solutions, in an Arrhenius cell with small electrodes. The more concentrated solutions were measured in a cell of inverted Y-shape, the electrodes fused into

[1] Archibald: *Trans. N. S. Inst. Sci.*, **9**, 291 (1897) and 307 (1898); McKay: *Ibid.*, 321 and 348 (1898).

the lower extremities. Bridge-wire and rheostat were calibrated. Temperature, 25° C.; conductivity corrected for slight variations. Specific conductivity is that of a cube of 1 cm. edge expressed in reciprocal ohms. Conductivity of the water used (1.7 to 3×10^{-6}) has been subtracted. Most of the results are the mean of at least two portions of the solution, several readings, at different points on the bridge-wire, having been made with each portion.

As Table II shows, the specific conductivity of ammonium sulphate in concentrations 0.75 and 1.5 is but little affected by saturating with calcium sulphate, while the conductivity of ammonium sulphate of concentration 3.0 saturated with calcium sulphate (conc. = 0.033) is about 1.5 per cent. *less* than that of the ammonium sulphate alone. The dilution due to water of the gypsum and expansion on dissolving the latter amounts to only about 0.2 per cent., so that the decrease in conductivity apparently is caused by the formation of complex ions having lower migration-velocity than those of ammonium sulphate. A blank experiment with concentrated ammonium sulphate solution and no gypsum showed no such falling-off in conductivity.

TABLE II.—CONDUCTIVITY OF AMMONIUM SULPHATE SOLUTIONS SATURATED WITH CALCIUM SULPHATE.

Concentration (*a*) $(NH_4)_2SO_4$ (*b*) $CaSO_4$.	Specific conductivity of single solutions.	Specific conductivity of mixture. Observed.	Means.	Calculated by isohydric method.	Decrease if non-dissoc. $CaSO_4$ constant. Per cent.
(*a*) 0.000					
(*b*) 0.01530	0.002214				
(*a*) 0.000977	0.0002822	I 0.002391	0.002394	0.002375	0.2
(*b*) 0.01500		II 0.002397			
(*a*) 0.001953	0.0005475	I 0.002545	0.002546	0.002545	0.3
(*b*) 0.01466		II 0.002547			
(*a*) 0.007812	0.002025	I 0.003598	0.003602	0.003610	1.6
(*b*) 0.01327		II 0.003606			
(*a*) 0.01563	0.003801	I 0.005080	0.005085	0.005105	1.7
(*b*) 0.01218		II 0.005089			
(*a*) 0.03125	0.007083	I 0.008102	0.008106	0.00816	2.1
(*b*) 0.01131		II 0.008109			
(*a*) 0.0625	0.01306	I 0.01387	0.01388		
(*b*) 0.01058		II 0.01388			
(*a*) 0.1250	0.02391	I 0.02456	0.02457		
(*b*) 0.01069		II 0.02458			
(*a*) 0.2500	0.04332	I 0.04390	0.04389		
(*b*) 0.01187		II 0.04388			

Concentration (*a*) $(NH_4)_2SO_4$ (*b*) $CaSO_4$.	Specific conductivity of single solutions.	Specific conductivity of mixture. Observed.	Means.	Calculated by isohydric method.	Decrease if non-dissoc. $CaSO_4$ constant. Per cent.
(*a*) 0.7500	0.1090	I 0.1091	0.1091		
(*b*) 0.01712		II 0.1091			
(*a*) 1.500	0.1853	I 0.1845	0.1846		
(*b*) 0.02446		II 0.1846			
(*a*) 3.000	0.2688	I 0.2653	0.2652		
(*b*) 0.03305		II 0.2650			

The Roman numerals refer to the solutions similarly designated in Table I.

In the table above we have the conductivity actually observed compared with that to be expected if Arrhenius' method of isohydric solutions is applicable. The close agreement[1] indicates that the mixtures have the composition assigned them in making the calculations by that method, presupposing always that conductivity is a measure of dissociation and that the latter takes place only into the ions here assumed.

The last column of the table shows the amount by which the conductivity of the mixture would be lower than that calculated, if the concentration of non-dissociated calcium sulphate were the same throughout as in the saturated water solution. The figures result from a comparison of the dissociation of calcium sulphate, as shown by Table IV, with the dissociation as obtained by subtracting the concentration of non-dissociated calcium sulphate in saturated water solution from the observed solubility in the several dilutions. Of the five mixtures for which this comparison can be made, in all but the two most dilute the difference seems to be outside the limits of possible errors of measurement and of method of calculation. It is to be concluded, then, that in these cases, the concentration of the non-dissociated portion of the calcium sulphate does not remain the same as in the saturated water solution.

Formation of complex compounds by union between ammonium sulphate and calcium sulphate would tend to lower the observed conductivity, acting therefore in the same direction as would constant concentration of non-dissociated calcium sulphate. The agreement between conductivity observed and calculated

[1] The fact that when two such electrolytes as calcium sulphate and ammonium sulphate are mixed each leaves the dissociation of the other unaffected is purely empirical; the mass-law would lead to the contrary expectation. Compare A. A. Noyes: *Tech. Quart.*, **17**, 302 (1904). This Journal, **27**, R. 201 (1905).

indicates that little or no such union takes place below concentration 0.0625. Measurements made under MacGregor's direction in one or two similar cases lead to the same conclusion.

The following data describe the isohydric solutions into which the mixtures are resolvable, and by means of which the conductivity was calculated :

TABLE III.

Factitious isohydric solutions.

Actual concentration $(NH_4)_2SO_4$.	Concentration SO_4''.	1 mol $CaSO_4$. Volume.	$(NH_4)_2SO_4$. Mols.	$(NH_4)_2SO_4$. Volume.
0.0009766	0.00848	60.38	$\frac{16.67}{256}$	6.28
0.001953	0.00897	56.24	$\frac{17.06}{128}$	12.00
0.007812	0.01229	37.84	$\frac{18.84}{32}$	37.52
0.01563	0.01700	25.08	$\frac{20.53}{16}$	57.0
0.03125	0.02675	15.24	$\frac{22.1}{8}$	73.2

The data for drawing the ion-concentration-volume curves were obtained in the case of calcium sulphate from as yet unpublished conductivity measurements on supersaturated gypsum solutions, very kindly placed at the writer's disposal by Dr. G. A. Hulett of the University of Michigan. The value for the most concentrated solution ($v = 15.24$) was derived by extrapolation, the curve embodying Hulett's observations terminating at $v = 17.64$. The results all lie almost absolutely on this curve, and are of sufficient number to make but slight interpolation necessary in getting at the values of the table above. For ammonium sulphate, the measurements detailed in Table II were used. Interpolation for other concentrations than those measured was made graphically, plotting molecular conductivity as function of cube root of dilution. This curve, drawn on a large scale by means of a spline, was tested by treating known points as unknown, and getting their value by interpolation. The results in the two trials made were but 0.3 per cent. from the correct values; the interpolations actually used in the calculations would be more accurate, as they were made through decidedly shorter intervals.

Molecular conductivity at infinite dilution, 25° C., was taken as 277 for calcium sulphate, 311 for ammonium sulphate.

The falling-off in concentration of non-dissociated calcium sulphate with increasing concentration of ammonium sulphate, is shown by the following table, which gives in mols per liter, the composition of the mixtures (saturated solutions) formed by the isohydric solutions of Table III :

TABLE IV.

Total concentration $(NH_4)_2SO_4$.	Concentration SO_4''.	Concentration Ca''.	Concentration non-dissociated $CaSO_4$.
0.00	0.0080	0.0080	0.0073
0.0009766	0.00848	0.00768	0.00732
0.001953	0.00897	0.00739	0.00727
0.007812	0.01229	0.00617	0.00710
0.01563	0.01700	0.00520	0.00699
0.03125	0.02675	0.00462	0.00620

SUMMARY.

Calcium sulphate, at 25° C., is two-thirds as soluble in dilute (0.1 mol per liter) and twice as soluble in concentrated (3 mols per liter) ammonium sulphate solution as in water.

The specific electric conductivity of concentrated ammonium sulphate solutions is lessened by saturating with calcium sulphate.

Assuming that dissociation of ammonium sulphate takes place into $2NH_4'$ and SO_4'' and of calcium sulphate into Ca'' and SO_4'' only, and that the conductivity is a measure of such dissociation, the solubility of calcium sulphate in dilute ammonium sulphate solutions is greater than required by the mass-law.

The conductivity of the dilute mixtures may be accurately calculated by means of Arrhenius' principle of isohydric solutions. In the data obtained in these calculations, the concentration of non-dissociated calcium sulphate decreases with increasing ammonium sulphate.

The work as a whole is additional evidence of the fact that we are not yet in possession of all the factors necessary for reconciling the mass-law to the behavior of electrolytes.

The measurements above described were made in the chemical laboratory of the University of Michigan.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C., February, 1905.

ON THE RECIPROCAL REPLACEMENT OF THE METALS IN AQUEOUS SOLUTIONS.

By George McPhail Smith.

Received January 23, 1905.

Experiments, for the purpose of comparing the rates at which magnesium liberates hydrogen from various aqueous solutions, have recently been performed by Kahlenberg;[1] and at his suggestion, G. Fernekes[2] undertook to find out whether sodium and potassium would act in a similar manner towards aqueous solutions. On account of the violence of the reaction in their case, and because the metals are so easily oxidized, amalgams of sodium and potassium were used instead of the metals themselves.

Fernekes found that solutions of sodium, potassium, barium, and certain other chlorides, for example, are more slowly acted upon by sodium and potassium amalgams than is pure water. Furthermore, he found that the retardation of the rate of evolution of hydrogen by sodium or potassium amalgam is about the same for isotonic solutions of sodium chloride and potassium chloride. He did not think these results were in harmony with the ionic theory.

In his investigation, Fernekes, besides acting on sodium amalgam with solutions of sodium salts, also acted upon it with solutions of potassium salts, then with hydrochloric and nitric acids, and finally, with salts of ammonium, barium, calcium, and strontium. In this case, as has long been known, potassium, ammonium, barium, calcium and strontium are all capable of replacing sodium in sodium amalgam.

Fernekes also acted with potassium amalgam on solutions of sodium and potassium salts.

It has been shown in a former paper[3] that potassium is capable of replacing sodium in its amalgam from a solution of potassium *chloride*, as well as from a solution of potassium hydroxide or carbonate. This was not known before, and Kraut and Popp (see below) state in their article, that such is not the case. On the other hand, it has been shown in the same place that sodium is

[1] This Journal, **25**, 380 (1903); *cf.* also Roberts and Brown : *Ibid.*, **25**, 801.
[2] *Jour. Phys. Chem.*, **7**, 611 (1903).
[3] Smith: *Ibid.*, **8**, 212 (1904).

also capable of replacing potassium in potassium amalgam,[1] it being only necessary to act on potassium amalgam with a concentrated solution of sodium chloride.

Taking these facts into consideration, which Fernekes did not do, his results can readily be interpreted by the ionic theory. This has been done by the author.[2]

The reciprocal replacement of potassium and sodium is very interesting. It has long been known that potassium is capable of replacing sodium in sodium amalgam;[3] and Berthelot and others after him have called this replacement an anomaly. They explained it as the necessary consequence of the greater loss of energy undergone by potassium than by sodium in the formation of their respective amalgams.[4] That potassium in its amalgam might also be replaceable by sodium does not appear to have entered their thoughts.

From the electrochemical series, in which potassium is more electropositive than sodium, it was to be expected that the replacement of potassium in its amalgam by sodium would take place more readily than the reverse; and in a former paper[5] I have shown that this really is the case.

I have also shown that potassium and barium, as well as sodium and barium, are reciprocally replaceable in their amalgams.[6]

In attempting to bring about the replacement of barium in its amalgam by potassium, a solution of potassium chloride was first employed; and with indifferent success. But by acting on the amalgam with a solution of potassium hydroxide, the desired replacement was readily accomplished. In this case the hydroxyl ions of the solution tend, by mass action, to prevent the entrance there of more hydroxyl ions. The barium is, therefore, prevented from acting on the water of the solution; and, in order for it to get out of the amalgam, it must replace potassium in the solution—*i. e.*, potassium must enter the amalgam. The solubility product of the barium hydroxide formed is very soon exceeded in the

[1] The author has since found that this fact was discovered also, almost simultaneously, by W. Kettembeil, who prepared sodium amalgam from potassium amalgam by acting on the latter with a solution of sodium hydroxide. (*Cf. Jour. Chem. Soc.* [London], 1904, *Abstr. ii.*, 173).

[2] *Jour. Phys. Chem.*, **9**, 13-35 (1905).

[3] Kraut and Popp : *Ann. Chem.* (Liebig), **159**, 188 (1871).

[4] Frémy : "Encyclopédie Chimique," (1885), sub sodium, p. 17; W. Kerp : *Z. anorg. Chem.*, **17**, 296 (1898).

[5] *Jour. Phys. Chem.*, **9**, 22 (1905).

[6] *Ibid.*, **9**, 16-23.

strong potassium hydroxide solution, and it separates in solid form. This, of course, also favors the replacement of the barium in the amalgam by potassium, the concentration of the barium ions in the solution being kept at a minimum.[1]

In general, according to Nernst,[2] when one metal is immersed in the solution of a salt of another metal, the following relation must hold, in order for the second metal to be precipitated by the first :

$$\frac{RT}{n_1} ln \frac{P_1}{p_1} > \frac{RT}{n_2} ln \frac{P_2}{p_2},$$

or

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}};$$

where the index 1 refers to the first metal, 2 to the second metal, and where P_1 and P_2 are the electrolytic solution-pressures, p_1 and p_2 the osmotic pressures of the monovalent ions, and n_1 and n_2 the valencies of the metals in question.

From this it follows that the following conditions are favorable for the precipitation of the second metal :

(1) High osmotic pressure (*i. e.*, high concentration) of the ions of the second metal.

(2) Great electrostatic pull—*i. e.*, high solution pressure of the first metal, and low osmotic counter-pressure (or low concentration) of the ions of this metal.

It is conceivable that any two metals might be reciprocally replaceable, depending on the relative magnitudes of $\sqrt[n_1]{\frac{P_1}{p_1}}$ and $\sqrt[n_2]{\frac{P_2}{p_2}}$ under different conditions; and at least one such pair of metals has been known for some time, *viz.*, mercury and silver.

[1] In this connection, the following data may be of interest. (*Cf. Jour. Phys. Chem.*, 9, 16-20.)

Barium amalgam (38.14g) was treated for one hour at the ordinary temperature with 25 cc. of a saturated solution of potassium hydroxide. There was no visible evolution of hydrogen, and considerable barium hydroxide separated in solid form.

The resulting amalgam gave:

0.1589g $BaSO_4$ (= 0.09354g Ba)
and 0.4104g K_2PtCl_6 (= 0.06614g K: equivalent to 0.1161g Ba)

The mother-liquor gave :

0.2038g $BaSO_4$ (= 0.11995g Ba).

i. e., 53.3 per cent. of the barium in the amalgam was replaced in one hour by potassium.

In an analogous experiment with 40 grams of the same amalgam and 50 cc. of saturated potassium chloride solution, only 0.0086g K_2PtCl_6 was obtained from the resulting amalgam.

[2] Nernst : *Theoret. Chem.*, **3**, *Aufl.* 668 and 674.

It is a well-known fact that mercury is capable of precipitating silver from a solution of silver nitrate. On the other hand, perhaps it is not so well known, that mercury can be precipitated from a solution of mercurous nitrate by silver;[1] and this process does not proceed anything like as readily as the first.

The following has also been known for some time[2] :

"Fügt man zum Kupfer im Daniellelemente eine hinreichend concentrirte Cyankaliumlösung, so werden die Kupferionen so weitgehend addirt, dass die elektromotorische Kraft der Kombination ihr Zeichen wechselt, d. h. in einer solchen Kombination geht Kupfer in Lösung und reduzirt das Zink.—Eine Reihe weiterer solcher Beispiele findet man bei Hittorf;[3] der zuerst derartige Fälle eingehender untersucht hat."

But in this case,—and the same applies to the cases described by Hittorf,[4]—there is an electric current to be taken into consideration; and, although zinc is reduced by copper, it is not precipitated on the copper pole, but on the zinc pole of the cell. Moreover, in this case, the copper and the zinc pole are immersed in solutions consisting essentially of potassium copper cyanide and of zinc sulphate, respectively.

The question now presented itself, whether metallic copper is capable of directly precipitating zinc from a zinc solution. It has been answered in the affirmative.

Reciprocal Replacement of Zinc and Copper.—That zinc will precipitate copper, even from a very dilute solution of copper chloride, for example, is very well known. By keeping the concentration of copper ions in a solution sufficiently low, and at the same time providing for the presence there of a relatively high concentration of zinc ions, it has been found possible to precipitate zinc directly from the solution by means of metallic copper.[5] This replacement does not readily take place, however, because

[1] Ogg : *Chem. Centralblatt*, 1897, ii, 11; 1898, ii, 1077.

[2] Nernst : *Loc. cit.*, 672.

[3] *Ber. chem. Ges.*, **26, R.**, 128 (1893).

[4] Hittorf found that, in the combination

$$\rightarrow Ag \mid CNK, KNO_3, NO_3Ag \mid Ag,$$

a galvanic current is produced in the direction indicated by the arrow, when the poles are brought into contact by means of a wire. He also found that this current does not disappear if for the silver cathode, immersed in silver nitrate solution, a cathode of copper, cadmium, or lead, immersed in the solution of a salt of the metal in question, is substituted. The silver is here electropositive in regard to the metals named, and it is seen that their positions in the electrochemical series do not determine the direction of the current in this case.

[5] Cf. Smith : *Jour. Phys. Chem.*, **9**, 31 (1905).

in reality the concentration of the zinc ions in the solution is exceedingly low.

A piece of bright copper foil was allowed to stand in a solution of potassium zinc cyanide, made by dissolving freshly prepared zinc cyanide in as little of a concentrated solution of potassium cyanide as possible, and then adding a slight excess of this solution. For a long time the copper remained unaltered, but after a day a distinct, bright coating of zinc could be seen on the copper. After five days the coating, which was still very thin, was tested, and found to be metallic zinc.

The same deposit can be obtained , in the course of an hour, by heating the copper with the solution, in a water-bath.

Reciprocal Replacement of Cadmium and Copper.—When a piece of cadmium is immersed in a solution of copper chloride in water, a precipitate of copper immediately commences to form on the cadmium. The reverse replacement was brought about in the same manner as that of zinc.

To a concentrated solution of cadmium sulphate, in a test-tube, was added concentrated potassium cyanide solution, until the precipitate at first formed was completely redissolved. A freshly polished piece of copper foil was then dropped into the solution, and the whole heated for one-half hour in a water-bath. At the end of that time a bright coating of cadmium had been deposited on the foil.

Reciprocal Replacement of Iron and Mercury, etc.—Upon the addition of a solution of potassium ferricyanide to mercury there is an immediate action, which becomes still more apparent, if a little potassium hydroxide is also added. In either case a thin, stiff coating of silky, metallic luster forms on the surface of the mercury.

In the absence of potassium hydroxide, a precipitate similar to Prussian blue separates; in its presence ferric hydroxide is precipitated. This is probably a secondary product, since the first precipitate is decomposed by potassium hydroxide with the formation of potassium ferrocyanide and ferric hydroxide.

That mercury is soluble in potassium ferricyanide, both in the presence and absence of potassium hydroxide, was shown as follows :

I. A solution of 7 grams of potassium ferricyanide and 1.5 grams of potassium hydroxide in 150 cc. of water was added to 101 grams

of mercury, in an Erlenmeyer flask, and the mixture allowed to stand at the ordinary temperature, with occasional shaking. After two and one-half hours the solution had changed from a clear yellow, to an opaque, orange color. This was due to the formation of colloidal ferric hydroxide, a part of which had begun to separate out, and remained in suspension. In all, the mixture stood for seventy-seven hours. At the end of that time four layers could be distinguished; *viz.*, liquid mercury, finely divided mercury, ferric hydroxide, and solution. On shaking, the red precipitate went into suspension, and could be collected on a filter. It dissolved in hydrochloric acid with a yellow color, and the solution gave a dark blue precipitate with potassium ferrocyanide.

At the end of the above period, the solution was filtered off; it was still slightly alkaline, and was of a faint yellow color. A drop of it gave a dark blue precipitate with ferric chloride. This solution, when heated on a water-bath, gave a further deposit of ferric hydroxide; and, in order to remove this, the solution was evaporated to dryness, taken up in water, and filtered. The filtrate was again evaporated to dryness; it left a yellow residue, which consisted mainly of potassium ferrocyanide. This was treated with concentrated sulphuric acid, and the mixture evaporated just to dryness. The residue consisted mainly of anhydrous ferric sulphate, which had been formed as follows:[1]

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO;$$ and $$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + SO_2.$$

This residue went in solution only on long-continued heating with water. The solution was strongly acidified with sulphuric acid, and hydrogen sulphide passed in. The mercuric sulphide formed weighed 2.15 grams. This precipitate was dissolved in aqua regia, and the solution gave a bright deposit of mercury on copper foil.

II. To 102 grams of mercury was added a solution of 3 grams of potassium ferricyanide in 100 cc. of water, and the mixture allowed to stand, with occasional shaking, in a stoppered flask, for four days at the ordinary temperature. The liquid was then filtered.

The precipitate consisted of a dark blue substance, similar to Prussian blue, which ran through the filter on washing. It was

[1] Treadwell's "Analytische Chemie," 3 Aufl., p. 97; Roscoe and Schorlemmer, Vol. II, Pt. ii, (1891), p. 101.

decomposed by potassium hydroxide solution, with formation of ferric hydroxide and potassium ferrocyanide.

The filtrate was greenish yellow in color, and a drop of it gave with ferric chloride a dark blue precipitate. It was evaporated on a water-bath, and gave on heating a further precipitate, similar to the first. The filtrate on being evaporated to dryness left a residue resembling potassium ferrocyanide. It was treated with sulphuric acid, and the mixture evaporated just to dryness; the residue was heated over night with water on a water-bath. The resulting solution was treated with a little sulphuric acid, and then with hydrogen sulphide. The precipitate obtained was extracted with carbon bisulphide to remove the sulphur. Result: 0.2358 gram HgS.

The residue of mercury was examined for iron in both cases. It had every appearance of an amalgam, and must have contained iron, in small quantity. The finely divided particles were not magnetic; neither was the film on the surface of the mercury appreciably attracted by a magnet. After washing with sodium hydroxide, and then with water, the mercury was tested for iron. It was extracted with nitric acid, which immediately rendered the mercury mobile; the extract was evaporated to dryness, and the residue taken up in dilute hydrochloric acid. The mercury was removed with hydrogen sulphide, and the filtrate evaporated to dryness with the addition of a little nitric acid. Potassium ferrocyanide was then added.

In another test the mercury was expelled from a portion by heating it in a porcelain crucible. A trace of residue was left. This was treated with concentrated hydrochloric acid, and the mixture evaporated to dryness on a water-bath. Then a drop of potassium ferrocyanide was added.

In these tests only traces of iron were found, and once or twice not even that.

Since the mercury went in solution, even in the presence of potassium hydroxide, it must have been in the form of potassium mercuric cyanide.

From the foregoing the following reactions are probable:

$$(a)\ 4K_3Fe(CN)_6 + 6Hg = 6K_2Hg(CN)_4 + 4Fe;^1$$

[1] This reaction appears to be reversible. Iron turnings, which had been freed from oil by ignition, and then from oxide by treatment with hydrochloric acid, were heated for three hours in a water-bath with a solution of 1.04 gram mercuric cyanide and 0.52 gram potassium cyanide in 20 cc. water. The reaction proceeded very slowly, but at the end of

(*b*) $3K_3Fe(CN)_6 + 4Fe = Fe_4(Fe(CN)_6)_3 + 9K$;

(*c*) $9K_3Fe(CN)_6 + 9K = 9K_4Fe(CN)_6$;

and, in case potassium hydroxide was also added,

(*d*) $Fe_4(Fe(CN)_6)_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3$.

The transitory separation of metallic iron is further borne out by the fact that metallic iron gives, with potassium ferricyanide solution, a precipitate similar to the one obtained above, and that it gives with the same solution, in the presence of potassium hydroxide, a reddish precipitate of ferric hydroxide.

Potassium amalgam reduces potassium ferricyanide to potassium ferrocyanide; and, if the ferricyanide solution is present in excess, it acts upon the mercury as soon as all the potassium has been removed.[1]

Reciprocal Replacement of Mercury and Silver.—As is well known, silver is readily precipitated from a solution of silver nitrate by mercury.

In this case the reverse replacement has been brought about by acting on silver with various salts of mercury. These experiments are of especial interest, in that they tend to strengthen conclusions already arrived at by the conductivity method and others, as to the slight degree of dissociation of certain salts of mercury in aqueous solution.

In the following experiments samples of silver purified in various ways were used, and all gave similar results. The metal used in the experiments here described, however, was prepared by precipitating the silver from an aqueous solution of silver nitrate by means of pure granulated zinc. The excess of zinc was removed by the addition of hydrochloric and sulphuric acids to the mixture of silver and zinc, and digesting for twenty-four hours on a

this time the solution gave a greenish coloration with ferric chloride, to which a slight amount of hydrochloric acid had been added; and the metal upon being heated in a porcelain crucible with a bright copper lid, gave a slight deposit of mercury on the copper.

Potassium ferrocyanide has no perceptible action on mercury, either in the presence or absence of potassium hydroxide. This is readily explained by the fact that the ratio 1:2 does not hold for the potassium and cyanogen in this salt.

[1] Results in every way analogous to those obtained with mercury, were also obtained with silver. With copper, potassium ferricyanide solution alone gives a bright red deposit, which turns dark on exposure to the air. Treated with concentrated hydrochloric acid, this deposit leaves a faintly yellow residue. It is therefore not iron hydroxide.

In none of these cases have I succeeded in definitely confirming the presence of metallic iron in the reaction products. The smallest particles are not attracted by a magnet, although once or twice out of numerous trials fragments seemed to be slightly magnetic, while in the solution, but quickly lost this property, especially on being taken from the liquid. These exceptions are by no means convincing.

radiator.[1] The silver was washed by decantation, treated with ammonia and thoroughly washed again. It was then dried on a water-bath and finally ignited. Thus prepared it presented a spongy appearance.

The following experiments were performed:

(1) Five-tenths gram silver was heated for half an hour in a water-bath with 10 cc. of a solution of mercuric chloride, which at that temperature contained a slight excess of the solid salt. The metal was then thoroughly washed with hot water, dried, and finally heated in a porcelain crucible which was covered with a weighed piece of freshly polished copper foil. The crucible was held in a punctured asbestos plate and the copper lid was kept cool by placing upon it a 100 gram weight. The mercury expelled by the heat from the silver condensed on the copper foil, and the increase in weight of the latter gave the weight of mercury in the silver amalgam—in this case 0.15 gram.

(2) The same experiment was performed with 0.5 gram silver and 10 cc. of saturated mercuric cyanide solution. After having been heated for half an hour in a water-bath the metal was thoroughly washed with hot water and then tested as above. The deposit of mercury was unmistakable, but it weighed only 0.0010 gram.

(3) To 0.5 gram silver in a test-tube was added 3.3 grams potassium cyanide and 6.3 grams mercuric cyanide, and then 10 cc. water. Immediately on the addition of the water the silver turned dark, owing to the deposition of mercury on its surface. The test-tube was heated in the flame of a Bunsen burner until the salts were completely dissolved; it was then further heated in a water-bath. In all, the heating lasted half an hour. The resulting amalgam, which was semi-liquid, was treated as described under (1). The mercury deposited on the copper foil weighed 0.41 gram. This reaction is reversible, and will be found suitable for the study of an equilibrium, probably approachable from either side.

(4) An experiment was carried out with silver and mercuric nitrate, but the salt was hydrolyzed to such an extent that it was practically impossible to separate the porous silver from the yellow oxide which separated. The same experiment, carried out with a sample of silver which had been melted to a compact globule,

[1] A sample of the zinc used in the precipitation of the silver was treated as above, and it dissolved without leaving a residue.

showed, however, that silver is capable of precipitating mercury from this salt also.

(5) Finally, 10 cc. of a cold, saturated mercurous nitrate solution, which had been kept over a mixture of the solid salt and metallic mercury, was heated as above for half an hour with 0.5 gram silver. The metal was then thoroughly washed, dried and tested as described under (1). A deposit of mercury was obtained which weighed 0.2487 gram.

The reactions may be represented as follows:

(1) $2Ag + HgCl_2 = 2AgCl + Hg$.[1]
(2) $2Ag + Hg(CN)_2 = 2AgCN + Hg$.
(3) $2Ag + K_2Hg(CN)_4 = 2KAg(CN)_2 + Hg$.
(4) $2Ag + Hg(NO_3)_2 = 2AgNO_3 + Hg$.
(5) $2Ag + Hg_2(NO_3)_2 = 2AgNO_3 + 2Hg$.

The last reaction has been found suitable for the study of an equilibrium, which, however, is approachable from one side only.[2]

As was to be expected, the largest amount of mercury was obtained from the double cyanide of mercury and potassium. The relative amounts of mercury obtained from mercuric chloride, mercuric cyanide and mercurous nitrate are somewhat surprising at first glance. In aqueous solution the cyanide is the least dissociated of the three, and yet the amount of mercury obtained from it was over a hundred times as small as that obtained from either of the other two. This can, however, be explained as follows:

The solution of mercurous nitrate had a strongly acid reaction in the cold; when heated it was probably still farther hydrolyzed. The presence of free nitric acid facilitated the solution of silver, and at least a part of that which went into solution was replaced by mercury.

In the case of mercuric chloride, double chlorides of silver and mercury were probably formed, *e. g.*, according to the following equation:

$$3HgCl_2 + 2Ag = 2AgHgCl_3 + Hg.$$

This is supported by the fact that silver chloride is markedly soluble in a solution of mercuric chloride in water.

According to C. Jones,[3] when finely powdered silver is treated

[1] In this case some calomel was also formed; the resulting metal was darkened by ammonia.

[2] Ogg: *Loc. cit.*

[3] *Ber. chem. Ges.*, **27**, R. 781 (1894).

in the cold for several weeks with an excess of mercuric chloride a double salt is formed as follows:

$$HgCl_2 + Ag = HgAgCl_2.$$

He says that this salt is blackened by ammonia, and is decomposed by concentrated ammonium chloride solution, according to the following equation:

$$3HgAgCl_2 = Hg + Ag + 2AgCl + 2HgCl_2.$$

Reciprocal Replacement of Mercury and Platinum.—A solution of chlorplatinic acid when treated with mercury gives a precipitate of metallic platinum, which is not very soluble in the mercury.

The reverse replacement can be brought about by heating metallic platinum with a concentrated solution of potassium mercuric cyanide.

A strip of platinum foil which presented a total surface of about 1 sq. cm. was heated in a water-bath for five hours with an excess of concentrated potassium mercuric cyanide solution. The foil, which was much less bright than originally, was thoroughly washed, dried and then tested for mercury, as in the preceding experiments. A deposit of mercury weighing 0.0002 gram was obtained on the copper foil.

Reciprocal Replacement of Mercury and Gold.—When a solution of gold chloride is treated with mercury the gold is reduced and forms an amalgam with the excess of mercury.

If, on the other hand, metallic gold is heated with a solution of potassium mercuric cyanide, gold goes in solution and mercury is precipitated on the surface of the gold.

Thirty-three hundredths gram of porous gold, obtained by the ignition of gold amalgam at a bright red heat, was heated for half an hour on a water-bath with an excess of concentrated potassium mercuric cyanide solution. The amalgam was thoroughly washed with hot water and then analyzed. It gave a deposit of mercury which weighed 0.0065 gram.

Reciprocal Replacement of Silver and Gold.—A small piece of pure gold was dissolved in a little aqua regia and the solution evaporated to a thick syrup. This was taken up in a little water, and a piece of silver added. It was at once covered with a dark deposit. After a short time the silver was taken out and washed, first with water and then with ammonia. It was found to be covered with a bright, loosely adhering coating of metallic gold.

The reverse replacement was accomplished by heating a small piece of gold with an excess of a concentrated solution of potassium silver cyanide. After two hours' heating in a water-bath the gold was covered with a white deposit. This deposit was washed with water, then with ammonia, and again with water. It was then dissolved in nitric acid, and with this solution hydrochloric acid gave a precipitate which was soluble in ammonia and which returned on the addition of nitric acid to the ammoniacal solution.

SUMMARY.

An abbreviated electrochemical series of the metals reads as follows: +K, Na, Ba, Sr, Ca, Mg, Al, Zn, Cd, Fe, Co, Ni, Sn, Pb, Cu, Hg, Ag, Pt, Au —.

The author has shown the metals in the following pairs to be reciprocally replaceable in aqueous solution, the metal first named in each pair being under ordinary circumstances more readily replaceable by the second than the second by the first.

K–Na; K–Ba; Na–Ba; Zn–Cu; Cd–Cu; (Fe–Hg); (Fe–Ag); Hg–Ag; Hg–Pt; Hg–Au; Ag–Au.

It is the intention of the author to continue the study of reciprocal replacements, as well in the presence of mercury as in its absence.

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A NEW SYNTHESIS OF HYDRONITRIC ACID.

BY ARTHUR WESLEY BROWNE.

Received March 20, 1905.

SEVERAL methods for the preparation of hydronitric acid from inorganic hydrazine compounds have been described. Curtius[1] obtained a dilute solution of the acid by passing the gaseous reduction products of nitric acid through a solution of hydrazine hydrate. Angeli[2] prepared silver trinitride by adding a saturated solution of silver nitrite to a solution of hydrazine sulphate. Dennstedt and Göhlich[3] made use of the interaction of hydrazine sulphate and potassium nitrite. Sabanejeff and Dengin[4] heated

[1] *Ber. chem. Ges.*, **26**, 1263 (1893).
[2] *Atti. d. Reale Accad.* (5), **2**, I, 569; *Centrbl.*, II, 559 (1893).
[3] *Chem. Ztg.*, **21**, 876 (1897); *Centrbl.*, II, 1093 (1897).
[4] *Ztschr. anorg. Chem.*, **20**, 21 (1899).

hydrazine sulphate with nitric acid. Tanatar[1] treated hydrazine with nitrogen trichloride, and later[2] oxidized a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution by treating with each of the following: chromic acid, hydrogen peroxide, bromine water, permanganic acid, lead dioxide and read lead.

ON THE REACTION BETWEEN HYDROGEN PEROXIDE AND HYDRAZINE SULPHATE IN PRESENCE OF SULPHURIC ACID.

Hydronitric acid may be obtained in considerable quantity by the action of hydrogen peroxide upon hydrazine sulphate in acid solution.[3]

The hydrazine sulphate used in the experiments to be described in the following pages was obtained from Kahlbaum (Berlin, S. O.). The percentage of sulphur was determined in four different samples of the compound by precipitating with excess of barium chloride and weighing the barium sulphate formed. Found: 24.36, 24.62, 24.39 and 24.31 per cent.; theory, 24.63 per cent.

The hydrogen peroxide solution was obtained from the Mallinckrodt Chemical Works (New York). The strength of this solution was determined at six different times during the course of the experiments by titration with potassium permanganate in acid solution. Between 3.02 and 3.07 per cent. of anhydrous hydrogen peroxide were found in the different samples taken.

The following procedure was adopted in the experiments. The weighed sample of hydrazine sulphate was in each case dissolved in water, acidified with sulphuric acid and put into a 300 cc. distilling flask. The hydrogen peroxide was then added and the solution was gently heated until the larger part of the water had distilled over into the receiver. In Expts. 6 and 7, 5 cc. of hydrogen peroxide were taken at the outset and 15 more were added through a separatory funnel during the course of the distillation. In each of the eleven experiments an additional 5 cc. of hydrogen peroxide and 5 cc. of water, not recorded in the table, were added toward the close of the experiment, and distillation was continued to insure complete separation of the hydronitric acid. Still

[1] *Ber. chem. Ges.*, **32**, 1399 (1899).

[2] *Ibid.*, **35**, 1810 (1902).

[3] This contradicts the statement made by Tanatar (*Loc. cit.*, **35**, 1810), after referring to the method of Sabanejeff and to his own earlier method for the preparation of hydronitric acid: "Sonst ensteht diese Säure nicht bei der Einwirkung von Oxydationsmitteln, weder auf Hyrazin noch auf Hydroxylamin allein."

further addition of both hydrogen peroxide and water after the second distillation had been completed was found to yield no hydronitric acid, except in the one case of Expt. 4, in which case the yield was accordingly not determined.

The results of the experiments were as follows:

No.	$N_2H_4.H_2SO_4$. Gram.	H_2O. cc.	H_2O_2. cc.	H_2SO_4. cc..	AgN_3 obtained. Gram.	Yield. Per cent.
1.	0.3497	10	30	5 2N	0.0518	19.28
2.	0.4625	25	50	10 2N	0.0404	11.37
3.	0.4618	25	50	10 2N	0.0426	12.01
4.	0.4993	25	10	10 2N	.....	.....
5.	0.5000	25	10	10 2N	0.0616	16.04
6.	0.5008	25	20	10 2N	0.0710	18.45
7.	0.5014	25	20	10 2N	0.0710	18.43
8.	0.5012	25	25	10 conc.	0.0958	24.88
9.	0.5004	25	25	10 conc.	0.1044	27.15
10.	0.5000	40	10	10 conc.	0.1090	28.37
11.	0.5008	25	10	25 conc.	0.1092	28.38

From Expts. 2 and 3 it is apparent that when a considerable excess of hydrogen peroxide was taken, the yield of hydronitric acid became smaller. From Expts. 8, 9 and 10 it is apparent that when the amount of sulphuric acid was increased the yield of hydronitric acid became larger. From a comparison of Expts. 10 and 11 it is seen that still further increase in the acidity of the solution was not accompanied by appreciable increase in the yield of hydronitric acid.

In order to prove that the acid obtained was identical with hydronitric acid a comparatively large amount was prepared by using ten times the quantity of materials taken in Expt. 10. The acid was concentrated by redistillation. Even in very dilute solution it possessed the unbearable, headache-producing odor characteristic of hydronitric acid. The white precipitate obtained by treating the redistilled acid with silver nitrate solution was completely soluble in dilute nitric acid.[1] When the washed precipitate, suspended in distilled water, was exposed to bright sunlight (in January) for ten minutes it was but very slightly darkened. Exposed in this way for a much longer time it gradually became gray in color. The dried precipitate exploded with violence when thrown upon a hot iron plate, or when touched with a glowing platinum wire. Particles weighing even less than 1 mg. exploded under these conditions with a sharp little snap. A few

[1] Dennis: This Journal, **18**, 947 (1896).

particles of the silver salt suspended in a little water sufficed to give the characteristic ferric chloride test,[1] which was also readily given by the acid itself. The red solution was in either case quickly decolorized by a few drops of 2 N hydrochloric acid, but was not decolorized by a few drops of 2 per cent. mercuric chloride solution.[2]

The percentage of silver in the silver salt was determined as an additional check upon the foregoing qualitative tests. A quantity of the substance was prepared by treating the acid with an excess of silver nitrate solution, and was washed by decantation until the wash-water gave no test for silver. The precipitate, suspended in a little water, was then transferred to two weighed platinum crucibles, was dried to constant weight over concentrated sulphuric acid in a vacuum desiccator and was weighed. Ten cc. of distilled water and 10 cc. of concentrated hydrochloric acid were then poured into each crucible, the solutions were evaporated to dryness at 100° and the silver chloride was dried to constant weight at a somewhat higher temperature. The amount of residue left on evaporating to dryness samples of the hydrochloric acid and water used in the analyses was next determined. The residue left after the evaporation of 10 cc. of hydrochloric acid and 10 cc. of water weighed 0.00025 gram. This amount was subtracted from the gross weight in order to obtain the true weight of silver chloride. (1) 0.1135 gram of the silver salt gave 0.10845 gram silver chloride. (2) 0.1306 gram of the silver salt gave 0.1248 gram silver chloride. This corresponds to 71.9 and 71.9 per cent. silver; theory, 71.9 per cent.[3]

The percentage yields of hydronitric acid obtained by the action of hydrogen peroxide upon hydrazine sulphate have been cal-

[1] Dennis and Browne: This Journal, **26**, 577 (1904).

[2] Dennis and Browne: *Loc. cit.*

[3] It may be of interest to state that the atomic weight of nitrogen calculated from these analyses, assuming that the atomic weight of silver (O = 16) is 107.93 and that the atomic weight of chlorine is 35.45, is in each case 14.04. This result is identical with the value given in the last report of the International Committee on Atomic Weights (this Journal, **27**, 5 (1905)), and is higher than the results (mean, 13.903) recently obtained by Miss Aston in the laboratory of Professor Ramsay (*Verhandlungen der Versammlung deutscher Naturforscher und Aerzte, 1903*, **1**, 62–74; *Chem. Centralbl., 1904*, **1**, 977). The authors's analyses were not made with any idea of obtaining accurate data concerning the atomic weight of nitrogen, nor are they to be considered as final in any sense, since the amounts of silver trinitride employed in the analyses were rather too small to insure accuracy in the second decimal. The author plans, in coöperation with Professor Dennis, to make in the near future a thorough study of the atomic weight of nitrogen in different salts of hydronitric acid. Professor Ramsay has kindly expressed to us his willingness that we should continue the investigation commenced in his laboratory.

culated (see table, last column) on the basis of the equation

$$3N_2H_4 + 5H_2O_2 = 2HN_3 + 10H_2O.$$

This seems to be the simplest and, on the whole, most plausible equation to express the reaction. It may be possible, however, that there are first formed unstable intermediate products that are subsequently decomposed so as to form hydronitric acid. If for example, the hypothetical "buzylene," $NH_2.NH.N:NH$ (of which the phenyl hippuryl derivative has been prepared by Curtius[1]), should be formed by the partial oxidation of two hydrazine molecules it is probable that it would readily decompose in presence of additional hydrogen peroxide, yielding hydronitric acid as the principal product of its decomposition.

SUMMARY.

Hydrazine sulphate and hydrogen peroxide react in presence of sulphuric acid, yielding hydronitric acid. Under certain conditions (see table, Expts. 10 and 11) the yield of hydronitric acid amounts to over 28 per cent. of theory.

All previous methods for obtaining hydronitric acid from hydrazine compounds have been based upon the reaction, under proper conditions, of these compounds with such substances as nitrous acid, potassium nitrite, silver nitrite, nitrogen trichloride, nitric acid and hydroxylamine chloride, all of which contain nitrogen.

The method described in the preceding pages is of theoretical interest, because it is the first method that has been suggested for the formation of hydronitric acid by the action, upon hydrazine, of a compound containing no nitrogen.

Further experiments in this laboratory have shown that hydronitric acid may be obtained in small quantites by the action upon hydrazine sulphate of certain oxidizing agents other than hydrogen peroxide, some of which have been previously used by other investigators in the quantitative determination of hydrazine. In a future communication a detailed account of these experiments will be given.

In concluding, the author wishes to express his gratitude to Prof. L. M. Dennis for the interest he has shown in this work, and for the suggestions he has offered during its prosecution.

CORNELL UNIVERSITY,
March, 1905.

[1] *Ber. chem. Ges.*, **26**, 1263 (1893).

EXPERIMENTS ON THE ACCUMULATION AND UTILIZATION OF ATMOSPHERIC NITROGEN IN THE SOIL.

By Edward B. Voorhees and Jacob G. Lipman.

Received March 7, 1905.

OBJECT OF THE EXPERIMENTS.

These experiments were arranged so as to bring out the relation of leguminous crops, such as cow peas, to the soil nitrogen; and to determine as far as practicable, the value of this leguminous crop as a source of nitrogen to subsequent, non-leguminous crops.

With this end in view, a soil was employed that contained an abundance of phosphoric acid and potash; and was, moreover, rather light in character, a condition that would favor the decay of organic substances. This soil originally consisted of equal parts by weight, of shale and quartz sand, and contained 0.09842 per cent. of nitrogen in the air-dry state. It was previously used for vegetation experiments in square wooden boxes during three seasons, and at the end of that time, the soil nitrogen had diminished very considerably. After these experiments, the soils from the several boxes were thoroughly mixed, and 160-pound portions were weighed off, and placed in each of the several boxes, hence there was in each box, a medium sandy soil, rich in mineral plant-food. Nitrogenous manures were added or withheld according to the following plan of study :

(1) The study of the source of nitrogen to cow peas under the following conditions:

(*a*) The addition of no nitrogen.

(*b*) The addition of different amounts of nitrate-nitrogen.

(*c*) The addition of different amounts of dried blood nitrogen.

(*d*) The addition of different amounts of ammonia-nitrogen in ammonium sulphate.

(*e*) The addition of different amounts of cow manure-nitrogen.

(2) The availability of cow-pea nitrogen, as compared with nitrate, organic (in dried blood), ammonia, and manure-nitrogen for the growth of the non-legumes.

(3) The possible accumulation of nitrogen in cultivated, but uncropped soils.

The wooden boxes used here were numbered from 1 to 54, inclusive, and only the first thirty were employed during the first season. Accordingly they received:

Boxes 1, 2, 3.....Nothing.
" 4, 5, 6.....1 gram of nitrogen as nitrate of soda.
" 7, 8, 9.....2 " " " " " " " "
" 10, 11, 12.....1 " " " " dried blood
" 13, 14, 15.....2 " " " " " "
" 16, 17, 18.....1 " " " " ammonium sulphate.
" 19, 20, 21.....2 " " " " " "
" 22, 23, 24.....1 " " " in solid and liquid manure.
" 25, 26, 27.....2 " " " " " " " "
" 28, 29, 30.....Nothing, and were kept bare.

The fertilizers and manure were applied to the respective soils July 5, 1902; 20 seeds of black-eyed cow pea were planted in each box, with the exception of 28, 29 and 30, and 8 quarts of water were added to supply the initial moisture.

The growth during the season was fairly uniform. At the end of the summer the cow peas were harvested, dried and ground, and after aliquot portions were taken for analysis, the ground material was kept dry in the laboratory. In the spring of 1903, millet was planted in the several boxes, which had been treated as follows:

Boxes 1 to 27, inclusive, received each the corresponding ground cow-pea crop of 1902.

Boxes 28, 29, 30....received no application of nitrogen.
" 31, 32, 33.... " 1 gram nitrogen in nitrate of soda
" 34, 35, 36.... " 2 " " " " " " "
" 37, 38, 39.... " 1 " " " dried blood.
" 40, 41, 42.... " 2 " " " " "
" 43, 44, 45.... " 1 " " " sulphate of ammonia.
" 46, 47, 48.... " 2 " " " " " "
" 49, 50, 51.... " 1 " " " solid and liquid manure, fresh.
" 52, 53, 54.... " 2 " " " solid and liquid manure, fresh.

Each box received May 29, 1903, 1 teaspoonful of barnyard millet seed, but the germination being poor, another teaspoonful of millet seed was added, about ten days later.

THE NITROGEN IN THE COW-PEA CROP.

The following table shows the amount and composition of the cow-pea crop obtained from the several boxes.

The analytical data presented in the above table show that the application of nitrogen resulted in every case (with the exception of 17), in a slight increase in the nitrogen content of the crop. At the same time, even the greatest increase, was but silght. To be sure, a portion of the nitrogen applied was apparently utilized, if we assume that the fixation was the same in each soil series—an assumption scarcely supported by the complete analytical data. At best, the addition of the ready, available nitrogen did not encourage the plants to make a more extensive use of the soil nitrogen, which is also shown in the soil analytical data obtained. A reference to the cylinder experiments on non-leguminous crops carried on by this Station,[1] will show that at least 70 per cent of the nitrate nitrogen applied became available to the crop in most cases, and the proportion available often reached 85 to 90 per cent. With the same methods of comparison, this does not seem to hold good with plants of the legume family. The averages of each series, as given in Table IV, show that only 30.3 per cent. of the nitrate nitrogen were utilized when 1 gram of it was applied, and only 18.9 per cent. when 2 grams were applied. The same is true of the highly available ammonia nitrogen. Where 1 gram of it was applied in 16, 17 and 18, only 23.7 per cent, and where 2 grams were applied, only 20 per cent. became available. The results are somewhat different where the organic nitrogen, either as dried blood or as manure, were employed. In 10, 11 and 12, where 1 gram of dried blood nitrogen had been applied, the availability reached 66.2 per cent., but with the double portion in 13, 14 and 15, the availability was reduced to 19.8 per cent., and, moreover, the absolute amount of nitrogen was less in the latter case than it was in the former. This would indicate that even large quantities of high-grade organic materials are a disadvantage to the fixation of nitrogen by leguminous crops. Where manure was added, the utilization of the applied nitrogen was apparently more thorough. With an application of 1 gram, there was an availability of 33.9 per cent., and with an application of 2 grams of manure-nitrogen, there was an availability of 37.1 per cent. In other words, the slowly available manure-nitrogen yielded

[1] N. J. Station Reports, 1889-1904.

TABLE I.

Box.	Fertilizer.	Nitrogen applied. Grams.	Weight of crop. Grams.	Nitrogen in crop. Per cent.	Nitrogen in crop. Grams.	Nitrogen increase over check. Grams.	Per cent. of nitrogen available.	Weight of residue of crop. Grams.	Nitrogen in residue. Grams.
1	Check	..	147	2.207	3.244	.....	....	122	2.69
2	"	..	137	2.467	3.380	.....	....	112	2.76
3	"	..	146	2.218	3.238	.....	....	121	2.68
4	Nitrate of soda	1	157	2.278	3.576	0.289	28.9	132	3.01
5	" "	1	159	2.225	3.538	0.251	25.1	134	2.98
6	" "	1	161	2.271	3.656	0.369	36.9	136	3.09
7	" "	2	158	2.193	3.465	0.178	8.9	133	2.92
8	" "	2	189	2.106	3.980	0.693	34.7	164	3.45
9	" "	2	156	2.274	3.547	0.260	13.0	131	2.98
10	Dried blood	1	164	2.401	3.938	0.651	65.1	139	3.34
11	" "	1	161	2.426	3.906	0.619	61.9	136	3.30
12	" "	1	170	2.355	4.004	0.717	71.7	145	3.41
13	" "	2	177	2.120	3.752	0.465	23.3	152	3.22
14	" "	2	161	2.176	3.503	0.216	10.8	136	2.96
15	" "	2	167	2.271	3.793	0.506	25.3	142	3.22
16	Ammonium sulphate	1	158	2.310	3.650	0.363	36.3	133	3.07
17	" "	1	139	2.352	3.269	0.018	....	114	2.68
18	" "	1	153	2.376	3.635	0.348	34.8	128	3.04
19	" "	2	152	2.397	3.643	0.356	17.8	127	3.04
20	" "	2	145	2.324	3.370	0.083	4.2	120	2.79
21	" "	2	183	2.239	4.097	0.810	40.5	158	3.54
22	Barnyard manure	1	154	2.369	3.648	0.361	36.1	129	3.06
23	" "	1	151	2.278	3.440	0.153	15.3	126	2.87
24	" "	1	152	2.493	3.789	0.502	50.2	127	3.17
25	" "	2	167	2.338	3.904	0.617	30.9	142	3.32
26	" "	2	185	2.525	4.671	1.384	69.2	160	4.04
27	" "	2	159	2.208	3.511	0.224	11.2	134	2.96

more to the cow-pea crop than the concentrated and highly available nitrate and ammonia-nitrogen; while with non-legumes the order of availability of the different materials is usually nitrate, ammonia, blood and manure-nitrogen, the order in this instance was blood, manure, nitrate and ammonia-nitrogen. If we consider the boxes where two grams of nitrogen were used, the order becomes manure, ammonia, blood and nitrate-nitrogen. The probable cause of these results will be discussed in connection with the soil analytical data.

TABLE II.

	Average percentage of nitrogen in crop.	Average nitrogen in crop. Grams.	Average percentage of applied nitrogen available.
1			
2	2.282	3.287	——
3			
4			
5	2.257	3.590	30.3
6			
7			
8	2.185	3.664	18.9
9			
10			
11	2.393	3.949	66.2
12			
13			
14	2.188	3.683	19.8
15			
16			
17	2.345	3.518	23.7
18			
19			
20	2.314	3.703	20.8
21			
22			
23	2.380	3.626	33.9
24			
25			
26	2.365	4.029	37.1
27			

This table shows that the cow-pea crop was proportionately richer in nitrogen in the series where only 1 gram of nitrogen was applied, as compared with the corresponding series where 2 grams were applied. Thus in 4, 5 and 6, the average percentage of nitrogen in the crop was 2.257 per cent., while in 7, 8 and 9, it was

only 2.185 per cent. Similarly in 10, 11 and 12, it was 2.393 per cent.; and in 13, 14 and 15, it was 2.188 per cent.; in 16, 17 and 18, it was 2.345 per cent., and in 19, 20 and 21, —2.314 per cent.; in 22, 23, 24, —2.380 per cent., and in 25, 26 and 27, —2.365 per cent. In 1, 2 and 3, where no nitrogen was applied, the plant substance was proportionately richer in nitrogen than was the plant substance in 4, 5, 6, 7, 8 and 9, where nitrate was applied.

The total nitrogen harvested in the crop was, with one exception, greater in the series where two grams of nitrogen were applied, as compared with the corresponding series where only 1 gram had been applied. The total nitrogen in the crop from 22, 23 and 24, where 1 gram of manure-nitrogen was applied, was greater than that in 4, 5 and 6, where 1 gram of nitrate-nitrogen was applied, and also greater than that in 16, 17 and 18, where 1 gram of ammonia-nitrogen was applied.

THE NITROGEN CONTENT OF THE BOX SOILS.

The analysis of the crops gave definite information as to the relation of the fertilizer applied to the yield. It was found with the quantities applied, that the soluble and easily available forms were not as advantageous to the cow-pea crop, as the slowly available, organic nitrogen. In other words, the relations here were different than in the case of non-legumes. In order to explain these differences, it becomes necessary to render a complete account, if possible, of the income and outgo of nitrogen, to determine the amount of nitrogen in the soil before and after the season's growth, and also the nitrogen added in the seed and in the water.

As stated above, each box contained at the beginning of the experiment, 160 pounds of air-dry soil, with 2.19 per cent. of hygroscopic moisture, an equivalent in round numbers to 71,000 grams of water-free soil. In the analysis of this soil according to the Kjeldahl method, 20 grams were taken for each determination, and five or six determinations were made of each sample. In each case there were at least three determinations, which agreed within 0.1 cc. of N/10 standard ammonia solutions, so that in most instances the limit of error due to the analytical operations was rather less than 200 mg. of nitrogen in the 71,000 grams of soil. Eight analyses were made of the soil, as it was at the beginning of the cow-pea experiment. It was found to contain on the water-free

basis, 0.07741 per cent. of nitrogen, or 54.96 grams of total nitrogen in each of the boxes. The twenty cow-pea seeds planted in boxes 1 to 27, inclusive, contained 71 mg. of nitrogen, and the water added during the season of growth contained 40 mg. of nitrogen.

After the cow-pea crop was removed, the soils were allowed to dry out in the boxes. A representative sample of each was then obtained by means of a soil-sampling tube, the samples were taken to the laboratory, air-dried, ground to pass through a 1 mm. sieve and their hygroscopic moisture determined. The several samples were found to contain the following amounts of hygroscopic moisture:

ORIGINAL SOIL, 2.19 PER CENT.

	Per cent.		Per cent.
1	1.19	16	1.17
2	1.20	17	1.20
3	1.26	18	1.20
4	1.20	19	1.19
5	1.32	20	1.19
6	1.10	21	1.11
7	1.16	22	1.08
8	1.25	23	1.03
9	1.08	24	1.06
10	1.16	25	1.59
11	1.19	26	2.61[1]
12	1.22	27	2.73[1]
13	1.29	28	1.33
14	1.19	29	1.03
15	1.24	30	1.00

THE NITROGEN CONTENT OF THE WATER-FREE BOX SOILS.

	Per cent.	Grams.		Per cent.	Grams.
1	0.08661	61.48	16	0.07964	56.54
2	0.08795	62.44	17	0.08596	61.02
3	0.08534	60.58	18	0.08396	59.60
4	0.08568	60.82	19	0.08228	58.42
5	0.08505	60.38	20	0.07962	56.52
6	0.08021	56.94	21	0.08088	57.42
7	0.08592	61.00	22	0.08552	60.70
8	0.08567	60.82	23	0.08148	57.84
9	0.08252	58.58	24	0.08534	60.58
10	0.08192	58.16	25	0.08630	61.26
11	0.08428	59.82	26	0.08754	62.14
12	0.08233	58.44	27	0.09103	64.62
13	0.09104	64.62	28	0.07906	56.12
14	0.08028	56.98	29	0.08182	58.08
15	0.08532	60.56	30	0.07956	56.48

[1] A slight amount of water got into the sample jar during the fire in the Experiment Station building, April, 1903.

The above figures show that the soil contained considerable quantities of nitrogen in proportion to the amounts applied. They also show that there was a gain of nitrogen in every soil, not excluding 28, 29 and 30, which were left uncropped. The gains are brought out more graphically in the following table, where the average amount of nitrogen in the crop and in the soil is given for each series.

The analytical results tabulated above show that the application of 1 gram of nitrogen resulted in a greater gain than the corresponding application of 2 grams. Thus, in 4, 5, and 6, there was an average gain of 6.97 grams of nitrogen in the soil and crop, while in 7, 8 and 9, where double the amount of nitrogen was applied, the total gain was only 6.72 grams of nitrogen. Similarly in 16, 17 and 18 there was a total average gain of 6.50 grams, and in 19, 20 and 21 there was a total average gain of 4.08 grams of nitrogen. In all of the soils, where either nitrate or ammonia was applied, the gain was much less than in the soils where no nitrogen salt was applied. This taken together with the fact that the application of the double portion of either nitrate or of ammonia, resulted in a smaller yield as compared with the single portion, shows clearly that the soluble nitrogen exerted a depressing effect on the process of fixation.

On the other hand, we find that the total average gain in 10, 11 and 12 was smaller than that in 13, 14 and 15, the corresponding amounts being 6.69 grams, and 7.33 grams. Similarly, in 22, 23 and 24, the average total gain was 7.26 grams, and in 25, 26 and 27, the corresponding gain was 9.63 grams. Here we find that the less soluble organic nitrogen was not detrimental to the fixation of atmospheric nitrogen, when applied in double the amounts.

Since the dried blood nitrogen is more readily available, that is, it becomes soluble sooner than the manure nitrogen, it should be of less advantage in the double portion to the leguminous crop than the corresponding double portion of the manure. As a matter of fact, we find that in the case of the dried blood, the increase from the double portion over the single portion is 0.64 gram of nitrogen, while the corresponding increase from the manure is 2.37 grams of nitrogen. The average gain in 10, 11 and 12 was 2.74 grams in the soil, and 3.95 grams in the crop, while in 13, 14 and 15 the average gain was 3.65 grams in the soil, and only

TABLE III.—THE INCOME AND OUTGO OF THE NITROGEN IN THE BOX SOILS.

Series.	Originally present. Grams.	Nitrogen in seed and water. Gram.	Nitrogen in fertilizer or manure. Grams.	Total nitrogen present at the beginning of the first season. Grams.	Total nitrogen present in soil at the end of the first season. Grams.	Average. Grams.	Gain in soil. Grams.	Nitrogen in crop. Grams.	Total gain. Grams.
1	54.96	0.115	.....	55.07	61.48	61.50	+6.42	3.29	9.71
2	54.96	0.115	.....	55.07	62.44				
3	54.96	0.115	.....	55.07	60.58				
4	54.96	0.115	1.00	56.07	60.82	59.45	+3.38	3.59	6.97
5	54.96	0.115	1.00	56.07	60.58				
6	54.96	0.115	1.00	56.07	56.94				
7	54.96	0.115	2.00	57.07	61.00	60.13	+3.06	3.66	6.72
8	54.96	0.115	2.00	57.07	60.82				
9	54.96	0.115	2.00	57.07	58.58				
10	54.96	0.115	1.00	56.07	58.16	58.81	+2.74	3.95	6.69
11	54.96	0.115	1.00	56.07	59.82				
12	54.96	0.115	1.00	56.07	58.44				
13	54.96	0.115	2.00	57.07	64.62	60.72	+3.65	3.68	7.33
14	54.96	0.115	2.00	57.07	56.98				
15	54.96	0.115	2.00	57.07	60.56				
16	54.96	0.115	1.00	56.07	56.54	59.05	+2.98	3.52	6.50
17	54.96	0.115	1.00	56.07	61.02				
18	54.96	0.115	1.00	56.07	59.60				
19	54.96	0.115	2.00	57.07	58.42	57.45	+0.38	3.70	4.08
20	54.96	0.115	2.00	57.07	56.52				
21	54.96	0.115	2.00	57.07	57.42				
22	54.96	0.115	1.00	56.07	60.70	59.70	+3.63	3.63	7.26
23	54.96	0.115	1.00	56.07	57.84				
24	54.96	0.115	1.00	56.07	60.58				
25	54.96	0.115	2.00	57.07	61.26	62.67	+5.60	4.03	9.63
26	54.96	0.115	2.00	57.07	62.14				
27	54.96	0.115	2.00	57.07	64.62				
28	54.96	0.04	.....	55.00	56.12	56.89	+1.89	.....	1.89
29	54.96	0.04	.....	55.00	58.08				
30	54.96	0.04	.....	55.00	56.48				

3.68 grams in the crop. The relations of the nitrogenous materials applied to the content of nitrogen in the soil are brought out in the following tabulation:

Nitrogen applied.	Nitrogen in the soil.
Nothing.	61.50 grams.
1 gram nitrogen in $NaNO_3$	59.45 "
2 " " " "	60.13 "
1 " " " dried blood.	58.81 "
2 " " " " "	60.72 "
1 " " " $(NH_4)_2SO_4$	59.05 "
2 " " " "	57.45 "
1 " " " manure.	59.70 "
2 " " " "	62.67 "

This tabulation also shows that after the removal of the crop the soils in the series where 1 gram of nitrogen was applied were poorer in nitrogen than those in the series where 2 grams were applied. Also in this case there is one exception, namely, in the case of the ammonia-nitrogen. Here the application of 2 grams of readily available ammonia-nitrogen, while it did not reduce the yield, discouraged the utilization of atmospheric nitrogen. The soil here contained a slightly greater amount of nitrogen after the removal of the crop, than it contained immediately after the application of the fertilizer, and while, on the whole, there was utilization of atmospheric nitrogen even in this case, the utilization was more limited, and the behavior of the cow pea was more like that of a non-leguminous crop. Apparently, the formation of tubercles and the utilization of the atmospheric nitrogen did not begin here until the readily available ammonia nitrogen had been largely used up. It will also be noticed, that there was a gain in the nitrogen content of the soil in the several series. The greatest gain was in 1, 2 and 3, 6.42 grams, almost double the amount contained in the crop. Hence the greater gain in the soil, 1, 2 and 3, more than offsets the increase in the nitrogen content of the crop from the other series. The following table brings out the relation of the several series in this respect :

Series.	Nitrogen in crop. Grams.	Increase over Series I. Grams.	Gain over nitrogen in soil. Grams.	Decrease over Series I. Grams.	Total decrease over Series I. Grams.
1	3.29	.....	6.42	.....	.....
2	3.59	0.30	3.38	3.04	2.74
3	3.66	0.37	3.06	3.36	2.99
4	3.95	0.66	2.74	3.68	3.02
5	3.68	0.39	3.65	2.77	2.38
6	3.52	0.23	2.98	3.44	3.21
7	3.70	0.41	0.38	6.04	5.63
8	3.63	0.34	3.63	2.79	2.45
9	4.03	0.74	5.60	0.82	0.08

The above results go far to show that the application of readily available, and concentrated nitrogenous materials to the growth of cow peas (and probably of other legumes) is very poor economy, indeed. Such applications may result in a slightly greater yield of crop, but they leave the soil poorer in nitrogen, and, therefore, less suitable for the growth of non-leguminous plants. The coarser organic materials seem to be much better suited for the purpose, and leave the soil in better condition. Hence, it would appear that where the supply of initial nitrogen for the growth of cow peas is desirable, the application of manure would be more advantageous than that of nitrate or ammonium salts.

It remains to note the gain of nitrogen in the uncropped soils, 28, 29 and 30. After subtracting the amount of nitrogen added in the water, namely, 0.040 gram, there still remains a gain of 1.89 grams. The gain is apparently due to nitrogen-fixing bacteria living in the soil independently of leguminous plants. The fixation of atmospheric nitrogen by such soil bacteria is discussed elsewhere[1], and need not be considered here. Without wandering too far into the realm of speculation, it would be of interest to consider, in this connection, whether these soil bacteria may add to the store of soil nitrogen, while leguminous plants are growing in this soil. If this should be so, the gain noted in the other series may be due, in part, to such bacteria, and a direct answer to this question can be obtained only by the use of pure cultures in these soil studies.

THE MILLET CROP OF 1903.

As stated above, the millet crop followed the cow peas in boxes 1 to 27, and was also seeded in the remaining boxes, 28 to 54, whose soils had been kept dry during the first season. The

[1] See N. J. Station Reports, 1903 and 1904.

TABLE IV.—MILLET, 1903.

Box No.	Fertilizer.	Nitrogen applied. Grams.	Air-dry weight of crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Average. Grams.	Average increase over check. Grams.
1	Cow-pea vines	2.69	210	1.328	2.669		
2	" " "	2.76	213	1.448	3.084	2.860	0.754
3	" " "	2.68	221	1.279	2.827		
4	" " "	3.01	208	1.328	2.762		
5	" " "	2.98	206	1.170	2.410	2.639	0.543
6	" " "	3.09	205	1.339	2.745		
7	" " "	2.92	217	1.557	3.379		
8	" " "	3.45	204	1.242	2.534	2.773	0.677
9	" " "	2.98	191	1.260	2.407		
10	" " "	3.34	190	1.283	2.438		
11	" " "	3.30	201	1.275	2.563	2.570	0.474
12	" " "	3.41	187	1.448	2.708		
13	" " "	3.22	194	1.208	2.344		
14	" " "	2.96	197	1.144	2.254	2.398	0.302
15	" " "	3.22	195	1.332	2.597		
16	" " "	3.07	205	1.201	2.462		
17	" " "	2.68	164	1.309	2.147	2.377	0.281
18	" " "	3.04	191	1.320	2.521		
19	" " "	3.04	204	1.305	2.662		
20	" " "	2.79	203	1.140	2.314	2.352	0.256
21	" " "	3.54	163	1.276	2.080		
22	" " "	3.06	231	1.422	3.285		
23	" " "	2.87	233	1.253	2.919	3.018	0.922
24	" " "	3.17	200	1.425	2.850		
25	" " "	3.32	195	1.455	2.837		
26	" " "	4.04	203	1.388	2.818	2.679	0.583
27	" " "	2.96	162	1.471	2.383		

TABLE IV (*Continued.*)—MILLET, 1903.

Box No.	Fertilizer.	Nitrogen applied. Grams.	Air-dry weight of crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Average. Grams.	Average increase over check. Grams.
28	Check	....	167	1.021	1.705		
29	"	....	216	1.118	2.415	2.096	.....
30	"	....	202	1.073	2.167		
31	Nitrate of soda	1.00	186	1.617	3.008		
32	" "	1.00	201	1.673	3.363	3.323	1.227
33	" "	1.00	197	1.827	3.599		
34	" "	2.00	200	1.718	3.436		
35	" "	2.00	230	1.707	3.926	3.652	1.556
36	" "	2.00	228	1.576	3.593		
37	Dried blood	1.00	215	1.564	3.363		
38	" "	1.00	217	1.422	3.086	3.179	1.083
39	" "	1.00	219	1.410	3.088		
40	" "	2.00	236	1.778	4.196		
41	" "	2.00	230	1.632	3.754	3.919	1.823
42	" "	2.00	221	1.722	3.806		
43	Sulphate of ammonia	1.00	254	1.823	4.630		
44	" "	1.00	220	1.684	3.705	4.403	2.307
45	" "	1.00	242	2.014	4.874		
46	" "	2.00	257	1.789	4.598		
47	" "	2.00	213	1.808	3.851	4.189	2.093
48	" "	2.00	244	1.688	4.119		
49	Solid and liquid manure	1.00	232	1.666	3.865		
50	" " " "	1.00	237	1.609	3.813	3.848	1.752
51	" " " "	1.00	193	2.003	3.866		
52	" " " "	2.00	196	2.134	4.183		
53	" " " "	2.00	258	2.329	6.009	5.297	3.201
54	" " " "	2.00	247	2.307	5.698		

Uncertainty as to identity of crop of boxes 7 and 54.
Mice did some damage to crop in boxes 3, 8, 12, 31, 34 and 49.

millet was harvested in the fifty-four boxes on August 1st, the crop dried, ground and analyzed in the customary manner. The amounts of dry matter and of nitrogen given in Table IV were found.

The facts brought out by these analytical data, are very instructive. It will be noted that there was a greater average yield, both of dry matter and of nitrogen in the second half of the entire series. Evidently the millet plants were able to secure more nitrogen from the fertilizer and the manure than from the ground cow-pea vines, even though the latter contained a greater amount of it. Moreover, the proportionate content of nitrogen in the millet crop was also greater in the second half of the series, thus showing again that there was more available nitrogen at the disposal of the crop in boxes 31 to 54 during the season's growth. Nothwithstanding the fact that the cow-pea vines had been finely ground before their incorporation into the soil, that the latter is light and well-aerated, and that plenty of moisture was provided, conditions which are all favorable to decay, the decomposition of the crop turned under was not rapid enough to furnish maximum amounts of soluble nitrogen. The subjoined tabulation shows the average yields in each series of three boxes.

TABLE V.—AVERAGE YIELDS IN THE MILLET CROP OF 1903.

	Dry matter. Grams.	Average of all. Grams.	Average per cent of nitrogen.	Average per cent of all.	Average amounts of nitrogen. Grams.	Average of all. Grams.
1	215		1.330		2.860	
2						
3						
4	206		1.281		2.639	
5						
6						
7	204		1.359		2.773	
8						
9						
10	193		1.331		2.570	
11						
12						
13	195		1.229		2.398	
14						
15		200		1.314		2.629
16	187		1.271		2.377	
17						
18						

Uncertainty as to identity of crop of boxes 7 and 34.
Mice did some damage to crop in boxes 3, 8, 12, 31, 34 and 49.

	Dry matter. Grams.	Average of all. Grams.	Average per cent of nitrogen.	Average per cent of all.	Average amounts of nitrogen. Grams.	Average of all. Grams.
19	190		1.238		2.352	
20						
21						
22	221		1.365		3.018	
23						
24						
25	187		1.432		2.679	
26						
27						
28	195		1.075		2.096	
29						
30						
31	195		1.704		3.323	
32						
33						
34	218		1.667		3.652	
35						
36						
37	217		1.465		3.179	
38						
39		221		1.704		3.767
40	229		1.711		3.919	
41						
42						
43	239		1.842		4.403	
44						
45						
46	238		1.760		4.189	
47						
48						
49	221		1.741		3.848	
50						
51						
52	234		2.261		5.297	
53						
54						

The above figures show that the average production of air-dry plant substance in boxes 28-54 was 221 grams as against 200 grams in boxes 1-27, or an increase of rather more than 11 per cent. Similarly, the average yield of nitrogen was 3.767 grams in boxes 28-54, as against an average yield of 2.629 grams in boxes 1-27. Furthermore, with one exception, the yield of air-dry plant substance and of nitrogen in boxes 1-27 was the greatest in Series 1 (1, 2, 3), where no nitrogenous manure had been applied at the

beginning of the experiment. Evidently, the previous manuring of the cow peas had no marked effect on the millet crop of 1903 and the nitrogen of the nitrate, dried blood and ammonium sulphate, applied in 1902, was altogether wasted. Conditions are rather different in boxes 28-54, where these materials were applied directly to the millet. Thus in boxes 28, 29 and 30, where no nitrogenous manure was used, the average yield of nitrogen in the millet crop was 2.096 grams, whereas, in boxes 31, 32 and 33, with one gram of nitrate nitrogen, the average yield was 3.323 grams, and in boxes 34, 35 and 36, with 2 grams of nitrate nitrogen, the average yield was 3.652 grams. Similarly, the yield with 1 gram of dried blood nitrogen was 3.179 grams, and with 2 grams of dried blood nitrogen it was 3.919 grams. With 1 gram of ammonium sulphate nitrogen, it was 4.403 grams, and with 2 grams of the same, only 4.189 grams; with 2 grams of manure nitrogen, it was 5.297 grams, as against 3.848 grams with 1 gram of manure nitrogen. The significance of these results will be discussed more fully in the following pages.

THE MILLET CROP OF 1904.

After the millet crop of 1903 was harvested, the soils in the several boxes were allowed to dry out, and were all kept under cover during the winter. In the spring of 1904, the soils were carefully stirred, moistened thoroughly, and on June 6th, millet was again seeded in each box without the further application of fertilizer materials. The seed germinated well, and the young plants grew rapidly. On August 8th, the millet was harvested and after air-drying was subsequently analyzed. Following are the analytical data.

TABLE VI.—MILLET, 1904.

Box No.	Air dry weight of crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Average. Grams.	Average increase over check. Grams.
1	128	1.126	1.431		
2	147	1.158	1.702	1.538	0.560
3	138	1.074	1.482		
4	124	1.090	1.352		
5	129	0.983	1.268	1.288	0.309
6	109	1.142	1.245		
7	116	1.190	1.380		
8	112	1.202	1.346	1.428	0.449
9	130	1.198	1.557		
10	135	1.090	1.472		

Box No.	Air-dry weight of crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Average. Grams.	Average increase over check. Grams.
11	129	1.011	1.304	1.419	0.440
12	128	1.158	1.482		
13	120	1.221	1.465		
14	120	1.074	1.298	1.367	0.388
15	120	1.114	1.337		
16	112	1.043	1.168		
17	105	1.214	1.275	1.246	0.267
18	120	1.078	1.294		
19	99	1.194	1.182		
20	109	1.106	1.206	1.082	0.103
21	80	1.074	0.859		
22	121	0.991	1.199		
23	114	1.186	1.352	1.240	0.261
24	105	1.113	1.169		
25	107	1.186	1.269		
26	113	1.186	1.340	1.362	0.383
27	116	1.273	1.477		
28	91	1.059	0.964		
29	93	0.999	0.929	0.979	.....
30	102	1.023	1.043		
31	112	1.301	1.457		
32	122	1.122	1.369	1.473	0.494
33	150	1.062	1.593		
34	142	1.178	1.673		
35	122	1.110	1.354	1.487	0.508
36	132	1.087	1.435		
37	118	1.349	1.592		
38	116	1.190	1.380	1.390	0.411
39	115	1.042	1.198		
40	157	1.210	1.900		
41	115	1.070	1.230	1.425	0.446
42	104	1.102	1.146		
43	122	1.090	1.330		
44	125	0.955	1.194	1.807	0.828
45	164	1.767	2.898		
46	134	1.178	1.579		
47	133	1.341	1.784	1.604	0.625
48	119	1.218	1.449		
49	144	1.309	1.885		
50	131	1.178	1.543	1.928	0.949
51	146	1.614	2.356		
52	182	1.699	3.092		
53	207	2.499	5.173	4.397	3.418
54	182	2.706	4.925		

In comparing the above with the corresponding results for 1903,

it becomes at once apparent that the yields in the earlier year were not only larger, but that the plant substance was richer in nitrogen than the corresponding material in 1904. Remembering that all other plant food constituents were present in abundance in 1904, as well as in 1903, the higher yields in the latter season were due to the greater amounts of available nitrogen, a fact brought out even more clearly in the following tabulation of the average yields in 1904.

TABLE VII.—AVERAGE YIELDS OF MILLET IN 1904.

	Dry matter. Grams.	Average of all Grams.	Average per cent. of nitrogen.	Average per cent. of all.	Average amounts of nitrogen. Grams.	Average of all. Grams.
1	138		1.115		1.539	
2						
3						
4	121		1.064		1.288	
5						
6						
7	119		1.200		1.428	
8						
9						
10	131		1.083		1.419	
11						
12						
13	120		1.140		1.367	
14						
15		118		1.127		1.330
16	112		1.111		1.246	
17						
18						
19	96		1.127		1.082	
20						
21						
22	113		1.097		1.240	
23						
24						
25	112		1.216		1.362	
26						
27						
28	95		1.030		0.979	
29						
30						
31	128		1.151		1.473	
32						
33						

	Dry matter. Grams.	Average of all Grams.	Average per cent. of nitrogen.	Average per cent. of all	Average amounts of nitrogen. Grams.	Average of all. Grams.
34	132		1.127		1.487	
35						
36						
37	116		1.198		1.390	
38						
39						
40	125		1.140		1.425	
41						1.832
42		132		1.388		
43	137		1.319		1.807	
44						
45						
46	129		1.236		1.604	
47						
48						
49	140		1.377		1.928	
50						
51						
52	190		2.314		4.397	
53						
54						

Also in 1904, the second half of the entire series (boxes 28-54), gave a higher average yield of dry matter and of nitrogen. At the same time there was a falling off in the yield throughout the whole series, due to the depletion of the more readily available nitrogen by the exhaustive crop of millet in 1903. In comparing the two, we find that there was a falling off in boxes 1-27, from 200 grams to 118 grams in the yield of dry matter, and a falling off from 2.629 grams of nitrogen to 1.338 grams. In boxes 28-54 there was a similar falling off from 221 grams of dry matter in 1903 to 137 grams in 1904, and a falling off from 3.767 grams of nitrogen to 1.832 grams. It will also be noted that the average yield of nitrogen in boxes 1, 2 and 3, where no nitrogen manure was applied in 1902, was, without exception, the largest for the first half of the series. The other yields seem to correspond in general with those of the preceding season. Thus, the average yield of nitrogen in boxes 4, 5 and 6, was greater than that in boxes 7, 8 and 9, in 1903, as well as in 1904. The same may be said of boxes 10, 11, 12 and 13, 14 and 15, and of boxes 16, 17, and 18 and 19, 20, and 21. Similar relations are brought out in the second half of the series.

THE AVAILABILITY OF THE NITROGEN IN THE GROUND COW-PEA VINES.

In boxes 1-27, where the ground cow-pea vines were applied in the spring of 1903, the succeeding crop of millet secured a part of its nitrogen from the decay of this ground material, and also from the decay of the cow-pea roots and stubble left in the ground. The amount of nitrogen thus obtained may be estimated by subtracting from the average yield in any series of three boxes, that obtained in boxes 28, 29 and 30 which had been kept bare in 1902, and were then used as checks in 1903 by being seeded to millet, without application of nitrogen. The following table shows the increase over the check plot in each series.

TABLE VIII.—INCREASE OVER CHECK PLOT.

Series.		1903. Grams.	1904. Grams.	Total. Grams.
1	1	0.764	0.559	1.323
	2			
	3			
2	4	0.543	0.309	0.852
	5			
	6			
3	7	0.677	0.449	1.126
	8			
	9			
4	10	0.474	0.440	0.914
	11			
	12			
5	13	0.302	0.388	0.690
	14			
	15			
6	16	0.281	0.267	0.548
	17			
	18			
7	19	0.256	0.103	0.359
	20			
	21			
8	22	0.922	0.261	1.183
	23			
	24			
9	25	0.583	0.383	0.966
	26			
	27			

Without exception, the largest increase in 1903, from the cow-pea vines and residues, was obtained in Series 1. In Series 3, with an initial application of 2 grams of nitrate-nitrogen, the increase

was greater than in Series 2, where the corresponding application was only 1 gram. The increase in Series 4 was greater than that in Series 5, and the increase in Series 6 was greater than in Series 7. In Series 8, where only 1 gram of manure nitrogen was applied in 1902, the increase was greater than that in Series 9, where 2 grams of manure nitrogen were applied. Comparing the yields in 1904 with those of 1903, we find in Series 1, a greater increase than in any other series. We also find that the increase in Series 3 was still greater than that in Series 2; the increase in Series 4 still greater than that in Series 5; and the increase in Series 6 still greater than that in Series 7. On the other hand, the increase in Series 9 was here greater than that in Series 8, while the reverse held true in 1903. Taking the total increase for the two years over the check plot, we find that Series 1 produced the greatest increase, and that Series 7 produced the smallest increase. The total average increase was highest for the manure plots, and then for the nitrate, dried blood, and ammonium sulphate plots in the order named.

AVAILABILITY OF THE NITROGENOUS MATERIALS APPLIED IN BOXES 31–54.

Series.	Nitrogen applied. Grams.		1903. Increase over check plot. Grams.	Nitrogen recovered. Per cent.	1904. Residual nitrogen recovered. Grams.	Total recovery. Per cent.
11	31, 32, 33	1	1.227	122.7	0.494	172.1
12	34, 35, 36	2	1.556	77.8	0.508	103.2
13	37, 38, 39	1	1.083	108.3	0.411	149.4
14	40, 41, 42	2	1.823	91.2	0.446	113.5
15	43, 44, 45	1	2.307	230.7	0.828	313.5
16	46, 47, 48	2	2.093	104.7	0.625	136.0
17	49, 50, 51	1	1.752	175.2	0.949	270.1
18	52, 53, 54	2	3.201	160.1	3.418	331.0

The data given here show that the nitrogen secured by the millet crop of 1903, was equivalent to 77.8–230.7 per cent. of that applied in the several nitrogenous materials. In only two cases was the recovery less than that contained in the fertilizer applied. On the other hand, the average amount of nitrogen contained in the crop from boxes 43, 44 and 45, was more than twice that applied. In the following year, another crop of millet was harvested without further application of nitrogen, and the amounts removed in this second crop, while by no means as large as in the previous season, were still very considerable. But the most striking feature of the crop of 1904, is the very large amount of nitrogen recovered in Series 18. The total average yield in this case was 4.397 grams of nitrogen as compared with 5.297 grams in 1903, yet the increase over the check plot was even greater in 1904 than it was in 1903, namely, 3.418 grams and 3.201 grams, respectively. Instead of becoming reduced in their nitrogen content, the soils in this series, unlike the soils in other series, actually supplied almost as much soluble nitrogen to the crop of 1904, as they supplied to the crop of 1903. Remembering that millet belongs to the crops incapable of utilizing the gaseous atmospheric nitrogen, it becomes possible to account for these extraordinary yields in two ways. Either the millet crop of 1904 was enabled in soils 52, 53 and 54, in some way, to utilize more thoroughly the nitrogen contained in the soil itself, than was true of the other soils, or atmospheric nitrogen was made accessible to it by nitrogen-fixing bacteria. A study of the following table, rendering a full account of the income and outgo of nitrogen in the several soils, will make this point clear.

The table contains a record of the nitrogen originally present in the soil, of that added from time to time in the seed, water and manure and fertilizer, of that added from the atmosphere by the cow peas and otherwise, of that removed in the two crops of millet, of that calculated to have remained in the soil, and of that actually present in the soil at the end of the three years' experiment. The initial amount of soil nitrogen, namely, 54.96 grams, was increased by the 100 mg. contained in the cowpea seed, by the 1 to 2 grams added in the fertilizer or manure, by the 100 mg. contained in the double quantity of millet seed in 1903, by the 50 mg. contained in the millet seed of 1904 and by the 120 mg. contained in the water used during the three seasons.

NITROGEN-BALANCE IN THE BOX SOILS.

Series.	Original in soil. Grams.	1902. In seed and water. Gram.	1902. In fertilizers and manures. Grams.	1902. Added from the atmosphere. Grams.	1903. In fertilizers and manures. Grams.	1903. In seed and water. Gram.	1904. In seed and water. Gram.	Total initial and added. Grams.
1	54.96	0.115	....	9.71–0.577	....	0.140	0.090	64.44
2	54.96	0.115	1.00	6.97–0.563	....	0.140	0.090	62.71
3	54.96	0.115	2.00	6.72–0.547	....	0.140	0.090	63.48
4	54.96	0.115	1.00	6.69–0.599	....	0.140	0.090	62.40
5	54.96	0.115	2.00	7.33–0.549	....	0.140	0.090	64.09
6	54.96	0.115	1.00	6.50–0.588	....	0.140	0.090	62.22
7	54.96	0.115	2.00	4.08–0.580	....	0.140	0.090	60.80
8	54.96	0.115	1.00	7.26–0.592	....	0.140	0.090	62.97
9	54.96	0.115	2.00	9.63–0.589	....	0.140	0.090	66.34
10	54.96	0.040	....	1.89	....	0.140	0.090	57.12
11	54.96	.....	....	....	1.00	0.140	0.090	56.19
12	54.96	.....	....	....	2.00	0.140	0.090	57.19
13	54.96	.....	....	....	1.00	0.140	0.090	56.19
14	54.96	.....	....	....	2.00	0.140	0.090	57.19
15	54.96	.....	....	....	1.00	0.140	0.090	56.19
16	54.96	.....	....	....	2.00	0.140	0.090	57.19
17	54.96	.....	....	....	1.00	.0 140	0.090	56.19
18	54.96	.....	....	....	2.00	0.140	0.090	57.19

NITROGEN REMOVED.

Series.	1903. Millet. Grams.	1904. Millet. Grams.	Total. Grams.	Calculated nitrogen in soil. Grams.	Actual nitrogen in soil. Grams.	Gain. Grams.
1	2.860	1.539	4.399	60.04	60.05	+.....
2	2.639	1.288	3.927	58.78	60.52	+ 1.74
3	2.773	1.428	4.201	59.28	59.59	+.....
4	2.570	1.419	3.989	58.41	59.32	+ 0.91
5	2.398	1.367	3.765	60.33	59.04	— 1.29
6	2.377	1.246	3.625	58.60	59.13	+.....
7	2.352	1.082	3.434	57.37	59.22	+ 1.85
8	3.018	1.240	4.258	58.71	60.15	+ 1.44
9	2.679	1.362	4.041	62.30	59.13	— 3.17
10	2.129	0.979	3.108	54.01	55.03	+ 1.02
11	3.323	1.473	4.796	51.39	55.12	+ 3.73
12	3.652	1.487	5.139	52.05	56.43	+ 4.38
13	3.179	1.390	4.569	51.62	59.31	+ 7.69
14	3.919	1.425	5.344	51.85	56.05	+ 4.20
15	4.403	1.807	6.210	49.98	58.28	+ 8.30
16	4.189	1.604	5.793	51.40	58.01	+ 6.61
17	3.848	1.928	5.776	50.41	60.89	+10.48
18	5.297	4.397	9.694	47.50	66.44	+18.94

By the conditions of the experiment, the treatment of the first half of the entire series, consisting of soils 1-30, was different from that of the second half of the series, which included boxes 28-54. In the former, there were three growing seasons accompanied by the various chemical, mechanical and biological changes, while in the latter, there were only two growing seasons. Besides, in boxes 1-27, the soil and manure nitrogen of 1902 became accessible to the millet crops of 1903 and 1904, only in so far as the cow-pea vines, into which it was incorporated, yielded it up again through the various processes of decay. The larger amounts of organic matter in these soils produced, of necessity, rather different soil conditions not merely by modifying the bacterial equilibrium in the soil, but also by affecting the solubility of the mineral constituents of the soil. As was already indicated, the cow peas converted the soluble soil and fertilizer nitrogen, as well as the atmospheric nitrogen, into insoluble proteid nitrogen, and the subsequent crops of millet could secure a portion of the latter only through a complicated series of bacterial changes. It should be remembered, however, that in such bacterial changes a part of the combined nitrogen is almost always transformed into free, gaseous nitrogen, and that the proportion of organic nitrogen, that may become available through decay, is usually less than one-half, and but seldom more than that. While it is not known how much nitrogen was set free through rapid oxidation of the organic matter in the different box soils, its amount in each case was probably not inconsiderable. This view is strengthened by the fact that the box soils are light and open, that the moisture conditions were always favorable for rapid decay, and that the temperature conditions were also favorable during the growing season. But whatever the amounts thus liberated, the final analyses show that, with two exceptions to be noted later, there was throughout a gain of soil nitrogen. Manifestly, then, by some process, or processes, in the soil itself, the loss of nitrogen was more than made up by the formation in the soil of nitrogen compounds at the expense of the free nitrogen of the atmosphere.

As to the amounts thus gained in the different soils, an examination of the above table will supply some interesting information. It will be noted that in Series 1 (boxes 1, 2 and 3) there was an average addition by the cow peas, and otherwise, of more than 9 grams of nitrogen per box. Hence, at the end of the first

season and at the beginning of the second season the average nitrogen content of these soils was rather more than 64 grams. The two crops of millet which followed the cow peas removed, in all, 4.398 grams of nitrogen, and the soil should have contained, at the end of the experiment, 60.04 grams of nitrogen. By actual analysis it was found to contain 60.05 grams, hence there was apparently neither a loss nor a gain of nitrogen in these soils, and the 4.399 grams of nitrogen secured by the two crops of millet were derived from the atmosphere by the legumes (cow peas), and with the decay of the latter the millet was enabled to find in the soil a quantity of nitrogen indirectly derived from the air. Nevertheless, in drawing this conclusion we should not overlook the fact already considered above, that in all processes of decay more or less of free nitrogen is returned to the atmosphere. For this reason there is much justification for the belief that the final analyses showing neither a gain nor a loss of nitrogen in Series 1, while they tell the truth, do not tell the whole truth. As a matter of fact, there was probably both a gain and a loss in these soils, and the two were so nearly balanced as not to affect the final results. Accepting this as a true interpretation of the conditions as they were, it would seem that the decay of the cow-pea residues and of the soil humus, involved nitrogen losses of unknown extent, losses that were offset by the fixation of atmospheric nitrogen in the soils in question.

In Series 2 (boxes 4, 5 and 6) there was, at the beginning of the second season, an average content of 62.48 grams (62.64 less 0.230 gram) of nitrogen made up of the initial nitrogen, and that added in the seed, water and cow-pea vines, stubble and roots. The two crops of millet withdrew 3.927 grams, leaving a theoretical balance of 58.78 grams of nitrogen. By actual analysis, however, the average amount found in this series was equivalent to 60.52 grams, thus showing a gain of 1.74 grams of nitrogen. Applying the above reasoning also in this case, it would appear that in this series the fixation of nitrogen counterbalanced the loss caused by decay, and even provided an excess of 1.74 grams of nitrogen. A similar comparison in Series 2, 3, 4, 5, 6, 7, 8 and 9 will show that there were gains in most instances and losses in two series. In seeking an explanation for the losses in these two series under conditions that led in the other series to distinct gains, we find that in Series 9, where the greatest loss had occurred,

there were present at the beginning of the second season more than 66 grams of nitrogen. In other words, the greatest loss occurred where the accumulation of nitrogen was greatest. Now, since the soil must be regarded as a culture medium where hundreds of bacterial species come into competition with one another in the struggle for food, it becomes clear that the decay bacteria will predominate in a soil well provided with nitrogenous organic matter, and that by this predominance they will either partly or wholly suppress the nitrogen-fixing bacteria. Such is undoubtedly the tendency in our arable soils, and the possibility, or even the probability, is not excluded, that the explanation given here is the true one, and more specific evidence in this direction is offered in the general discussion.

Before passing on to the consideration of Series 10-18 we should note again the effect of the manures and fertilizers in Series 2-9 on the final results. Considering that the average yield of 4.399 grams of nitrogen in the two millet crops on Series 1 was greater than the corresponding yield in any other of the first nine series, it becomes evident enough that the nitrogenous materials applied to the cow peas were more than wasted. From what we know of symbiotic fixation we are justified in the conclusion that the soluble nitrogen salts discouraged fixation, and hence led to a smaller gain of nitrogen in the soil. Taking the gains and losses in the final balance we find that in Series 2, where 1 gram of nitrate nitrogen was applied in 1902 there was a final gain of 1.74 grams of nitrogen, while in Series 3, where 2 grams of nitrate-nitrogen were applied, the final gain was only 0.31 gram. Similarly, there was a final gain of 0.91 gram in Series 4, and a corresponding loss of 1.29 grams in Series 5; a final gain of 1.44 grams in Series 8, and a corresponding loss of 3.17 grams in Series 9. The fact that there was not a greater final gain in Series 1 is probably due to the addition of such a large amount of nitrogen and of organic matter in the soils of this series by the cow-pea crop, and the fact that the final gain in Series 7 was greater than that in Series 6 is probably due to the comparatively small addition of nitrogen and of organic matter in the soils of this series by the cow-pea crop of 1902.

Passing on to the consideration of the other series, we find that in Series 10, comprising boxes 28, 29 and 30, where the soils were kept moist and bare during the first season, there was a very dis-

tinct gain of combined nitrogen. In the following season this was made the check series, and it raised a good crop of millet without addition of combined nitrogen. Another fairly good crop was raised on this series in 1904. The two crops contained 3.108 grams of nitrogen, while the soil itself was found to contain as much as was present at the beginning of the experiment, or even a little more. Allowing for the nitrogen added in the seed and in the water, we find that in these soils, kept bare throughout the first season and covered with exhaustive crops of millet in the following seasons, there was a gain of almost 3 grams of nitrogen without resort to symbiotic fixation by legumes. The amount thus gained is very considerable, as compared with the total initial amount of 54.96 grams. But, however important these gains, they are greatly exceeded by those made in the following series in the course of only two seasons. Taking, for instance, Series 11 and 12, we find that the initial nitrogen was increased in 1903 by 1 and 2 grams, respectively, of nitrate-nitrogen and also by that contained in the seed and water for the two years. These additions increased the initial and added nitrogen content to 56.19 grams and 57.19 grams, respectively. The two crops of millet raised contained 4.796 grams of nitrogen in Series 11, and 5.139 grams of nitrogen in Series 12. In other words, the additional gram of nitrate-nitrogen led to an increase of 0.379 gram of millet nitrogen, and assuming that this increase was entirely due to the greater quantity of nitrate the latter showed a recovery of almost 38 per cent. in the additional gram of nitrogen. Taking into account the amounts originally present in the soil, those subsequently added in one way or another, and those removed in the millet crops, there should have been left in the soil 51.39 and 52.05 grams of nitrogen in Series 11 and 12, respectively. The corresponding amounts found by actual analysis were 55.12 and 56.43 grams, respectively, leaving a gain of 3.73 grams of nitrogen in Series 11, and a gain of 4.38 grams of nitrogen in Series 12. Similarly, in Series 13, where 1 gram of dried blood nitrogen had been applied, there was a gain of 7.69 grams, and in Series 14, with an application of 2 grams of dried blood nitrogen, there was a final gain of 4.20 grams. The greatest gains, however, were found in Series 17 and 18, where 1 and 2 grams, respectively, of manure nitrogen were applied. Beginning with an initial quantity of nitrogen in the soil, seed and water of somewhat over 57 grams,

there was harvested in Series 18 an average quantity of nitrogen equivalent to 5.297 grams in 1903 and an additional quantity equivalent to 4.397 grams in 1904. The total yield in the two crops was, therefore, equivalent to 9.694 grams of nitrogen, or almost one-sixth of that supplied in the soil, manure, seed and water. Assuming that the transformation of the insoluble humus nitrogen into nitrate involved no liberation of uncombined nitrogen there should have been left in the soil at the end of the experiment 47.50 grams of nitrogen. By actual analysis it was found to contain 66.44 grams of nitrogen, or 9.25 grams more than was initially supplied. Adding to that the 9.694 grams found in the crops we obtained a total gain of 18.99 grams. This remarkable increase, almost one-third of that originally present or supplied, deserves careful study.

Assuming the nitrogen content of a fair arable soil to be 5,000 pounds per acre to a depth of one foot, an increase by one-third of this amount would mean more than 1,600 pounds of nitrogen per acre, and that in the course of only two short growing seasons. Further comparison reveals the fact that the fixation was greatest in the series where the greatest amount of manure was applied, and that the next greatest amount of nitrogen occurred in the series where the smallest quantity of manure was applied. Furthermore, the final gains thus secured represent an amount less than that actually present, for there probably was a more or less extensive volatilization of nitrogen from these soils in the course of decay. The final gain of 18.94 grams in Series 18, or the corresponding gain in any other series, thus becomes the algebraic sum of the gains and losses that had actually occurred.

Before proceeding to the discussion of the general significance of the facts established in this experiment, at least one other point should be mentioned. It will be noted in examining the detailed yields for 1903 that the parallels in each series agreed within fairly narrow limits. There are a few exceptions, however, wherein the discrepancies could only be ascribed to biological causes. Thus in the check Series 10 (boxes 28, 29 and 30), the yield in box 28 was only 1.705 grams of nitrogen, as compared with 2.4115 grams in 29 and 2.167 grams in 30. Similarly, in Series 15, the nitrogen yield in box 44 was only 3.705 grams, as compared with 4.630 and 4.874 grams, respectively, in boxes 43 and 45. Discrepancies of a like nature occurred also in some

of the other series. These discrepancies are, however, greatly exceeded in some series for the following season (1904). Thus in Series 14, we find that the yield in soil 40 was 1.900 grams of nitrogen, or more than a third in excess of that yield either in soil 41 or soil 42. In Series 15 soil 45 yielded in the millet crop 2.898 grams of nitrogen as compared with 1.330 grams and 1.194 grams in soils 43 and 44, respectively; and in Series 18 soil 52 yielded in the millet crop 3.092 grams of nitrogen, as compared with 5.173 and 4.925 grams in soils 53 and 54, respectively. All these differences show that even though the same conditions of temperature and moisture prevailed in each case, very striking variations in the yield occurred, and since the soils themselves showed no loss, but rather a gain of nitrogen, these variations could very properly be ascribed to bacteriological differences more or less far-reaching in their character.

DEFINITIONS.

In order to add clearness to the deductions drawn here it is deemed advisable to define some of the terms employed in this paper. The term *fixation* implies the transformation of the uncombined elementary nitrogen of the air into organic nitrogen compounds by the activities of certain bacteria known as nitrogen-fixing, or nitrogen-gathering bacteria. The fixation of nitrogen may be *symbiotic* or *non-symbiotic*. The term *symbiotic* is derived from the noun *symbiosis* and denotes the dwelling together of two distinct forms of life with mutual benefit resulting. This term is most frequently applied to the fixation of nitrogen by members of the legume family, such as clovers, peas, beans, etc., with the aid of certain bacteria, which form tubercles on the roots of these plants. Some investigators have claimed, however, that the bacteria inhabiting the legume tubercles represent an instance of parasitism rather than of symbiosis. The bacteria inhabiting the tubercles of the legumes enable them to make use of the elementary nitrogen of the air, whereas in the absence of these bacteria no tubercles are formed, and no fixation of nitrogen by the legumes can take place. It is believed that these tubercle bacteria when living in the soil outside of the legume roots can also fix nitrogen, but to a much more limited extent, and when thus living outside of the legume roots they become *non-symbiotic*.

Besides the legume tubercle bacteria there are two important

groups of soil bacteria which can fix very considerable quantities of atmospheric nitrogen. The first of these includes well-defined species of butyric ferments, which are *anaerobic*, that is, develop in the absence of oxygen. *Clostridium Pastorianum*, isolated by Winogradsky, belongs to this group. The second group include the genus *Azotobacter*, large bacilli possessing a pronounced nitrogen-fixing power and are *aerobic* in character (that is, requiring a plentiful supply of oxygen for their growth). The fixation of nitrogen by the members of these two groups is usually referred to as *non-symbiotic*, although a certain amount of symbiosis occurs also here. Unlike that of the legumes and tubercle bacteria, the symbiosis in this case is either with other bacteria or with algae, the latter being one-celled green plants.

GENERAL CONSIDERATIONS.

The facts established in this experiment are of very considerable practical importance, even though the experiment itself was carried out under conditions more or less artificial. They demonstrate, in no uncertain manner, that the bacterial activities that concern the gain and loss of nitrogen in the soil are manifold and complex, and yet susceptible of differentiation. Evidently, there was a gain of nitrogen in the box soils by means of symbiotic fixation where the cow-pea crop was grown. It is scarcely necessary in this place to review in detail the vast amount of work that has been devoted to the study of this phase of the subject, since Hellriegel and Wilfarth's publications,[1] but it may be said in general that the practical application of their discovery has been comparatively limited thus far. To be sure, leguminous crops were grown intelligently for the accumulation of nitrogen in the soil, even before their discovery,[2] and more extensive use has been made of legumes in crop rotation since their discovery. Nevertheless, as the recent studies of Hiltner[3] indicate, there is great promise of remarkable development in the production of *virulent* cultures of legume bacteria for purposes of soil inoculation. It will thus be seen readily that symbiotic fixation of nitrogen in the soil is not a constant quantity even under the same climatic conditions. As living things, the legume bacteria are affected

[1] "Untersuchungen über die Stickstoffnahrung der Gramineen und Leguminosen," *Z. des Vereins fur Rubenzuckerindustrie* d. D. R., November, 1888.

[2] Schultz-Lupitz, "Die Kalidüngung auf leichtem Boden," Berlin, 1883.

[3] *Centr. f. Bact. u. Par.*, Part II, **12**, 497.

by changing conditions within the plant, as well as outside of it, and their nitrogen-fixing power may be very considerably modified after they find their way out of the tubercles and back into the soil. When once there they may be weakened in the competition for food with other bacteria, and thus rendered incapable of as vigorous fixation as formerly. In this connection it is interesting to note that the tubercle bacteria may be able to fix atmospheric nitrogen outside of the legume tubercles, as was demonstrated, for instance, by Maze,[1] or recently by Chester.[2] It is not known whether in the present experiment there was any addition to the store of soil nitrogen by such action of the tubercle bacteria, but in the absence of defintie information on this point, and because of the fact that there was a nitrogen gain in soils 1-27, even after the removal of the cow-pea crop, it cannot be claimed that this *possibility* was excluded. With this reservation it must be admitted, however, that the *probability* of extensive fixation, having taken place in this manner, is not very great, and for the following reason: While there were some nitrogen gains in the cow-pea soils in 1903 and 1904, the gains were not as great as they were in boxes 31-54, where no cow peas were grown, and hence were not provided with as many tubercle bacteria.

As to the bacteria capable of fixing atmospheric nitrogen when growing alone in the soil, reference need only be made to the work of Berthelot,[3] Winogradsky,[4] Beyerinck,[5] Gerloch and Vogel,[6] Freudenreich,[7] and Lipman[8] to show their universal distribution. These bacteria, occurring, as they do, in most arable soils, have undoubtedly certain functions to perform there. In other words, since they are adapted to survive and to develop under conditions where the vast majority of ordinary decay bacteria would perish, they undoubtedly add to the combined nitrogen in the soil under such conditions. In the fine-grained, compact soil the anaerobic *Clostridium Pastorianum* and allied species play the more important rôle; in the lighter, open soils the members of the *Azotobacter* group are of greater importance. But it should be re-

[1] "Fixation de l'azote libre par le bacille des nodosites de legumineuses," *Ann. de l' Inst. Pasteur*, **11**, 1897.

[2] Bull. 66, Delaware Agr. Expt. Station.

[3] Chimie Vegetale et Agricole, p. 69.

[4] *Archives des sciences biologiques*, **3**, and *Centr. f. Bact. u. Par.*, Part II, **9**, 43.

[5] *Ibid.*, **7**, 561, and **9**, 3.

[6] *Ibid.*, **8**, 669.

[7] *Ibid.*, **10**, 514.

[8] N. J. Expt. Station Reports 1903 and 1904.

membered in this connection that the nitrogen-fixing bacteria, whether aerobic or anaerobic, must have food, and like other bacteria they rapidly disappear from soils devoid of organic matter. It is for this reason that in the box soils 52, 53 and 54 there was a large fixation of nitrogen. The organic matter of the manure, by offering the food, and hence the source of energy, to these bacteria, made possible their rapid development, and, therefore, also an intense fixation of atmospheric nitrogen. But it will be asked in this connection why it was that the organic matter of the cowpea vines and residues did not offer a similar source of food and energy. To this it may be answered that the bacterial equilibrium in the soil may be shifted in one direction or another, and no better illustration of this is needed than the studies of Hiltner and Störmer.[1] When the nitrogen content of the soil passes beyond a certain limit the decay bacteria increase rapidly and in the struggle for existence they are able, with the advantages at their disposal, to suppress the more slowly growing *Azotobacter* species. Hence, where large quantities of legume material are incorporated into the soil, as was done in the case of boxes 1-27, the nitrogen-fixing bacteria cannot develop as freely, and in the algebraic sum of the products the gaseous nitrogen liberated from the soil frequently more than offsets that combined and fixed in the soil by the nitrogen-gathering bacteria. It thus becomes evident that the best results from non-symbiotic nitrogen-fixation may be obtained in open soils, provided with adequate quantities of moisture, and with fairly large amounts of organic matter having a rather small nitrogen content. These conditions are most suitable for the development of the aerobic *Azotobacter* species.

It would not be out of place here to express the hope that with our broadening knowledge we shall find means to provide for a better conservation of the soil nitrogen, whether it be by soil inoculation with vigorous cultures of symbiotic and non-symbiotic nitrogen-fixing bacteria, or by an intelligent maintenance of the nitrogen balance in the soil, so as to prevent the unnecessary dissipation of combined nitrogen through the one-sided activities of the decay bacteria.

As to the practical application of the information already in our possession, this much should be said: We should remember

[1] Studien über die Bacterienflora des Ackerbodens, etc., Berlin, 1903.

that our knowledge of the bacteriological conditions in the soil is still so limited that a general and successful inoculation with non-symbiotic nitrogen-fixing bacteria, with the decay bacteria, or with nitrifying bacteria is entirely out of the question for the present. The only direction in which soil inoculation has been rendered more or less practicable is the inoculation with cultures of various tubercle bacteria. Such inoculation can, therefore, be applied to legumes and *legumes* only. By so doing we may make possible the formation of tubercles and, therefore, the fixation of nitrogen by leguminous crops in such soils where the proper bacteria are naturally absent, but it should also be remembered that in most soils the failure of leguminous crops to grow satisfactorily is due not to the absence of the proper soil bacteria, but to general unfavorable soil conditions, to absence of a sufficient amount of lime, of a sufficient amount of humus, or of sufficient aeration. The inoculation of such soils without previous improvement would be a waste of effort and money. There is ample justification, therefore, to utter here a warning against misconception and unjustifiable expectation. Ignorance in this direction will be exploited, as ignorance in other directions has been exploited, by attempts to sell to farmers, improperly informed, cultures of soil bacteria advertised as the panacea for all soil-ills. Let the man who wishes to inoculate his soil remember that it is not yet practicable to inoculate it for wheat or potatoes, or melons and while it is practicable to inoculate it for alfalfa, or soy beans, or other legumes, he should inform himself as to the real facts before proceeding with his inoculation.

[CONTRIBUTION FROM THE FOOD DIVISION OF THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE. SENT BY H. W. WILEY.]

EXAMINATION OF LARD FROM COTTONSEED-MEAL-FED HOGS, BY PHYTOSTEROL ACETATE METHOD OF BÖMER.

BY L. M. TOLMAN.

Received March 1, 1905.

THE fact that lard prepared from hogs fed on cotton-seed meal will give positive tests with the Halphen and the Becchi reagents has been known for some time. Consequently, a question of

adulteration is always raised when these tests are found to be given by any sample of lard.

Recently, Fulmer[1] published the results of some careful and complete feeding experiments on hogs where varying amounts of cottonseed meal were fed, the object being to determine its effect on the lard, especially as regards the Halphen test for cottonseed oil, and the results show that little value can be attached to the test in an examination of lard, especially where cottonseed meal is likely to have been fed.

Through the kindness of Mr. Fulmer, fifteen samples of lard, prepared from the hogs used in his experiments, were obtained for this work. In his paper he has carefully described these samples, in detail, so that only a brief description of them will be given in Table II. Solstein[2] has called attention to some samples of lard, which he obtained in Chicago, and which gave a strong Halphen test, but did not show the presence of phytosterol,and he concluded that this test was final.

The lards obtained from Fulmer were prepared from different parts of the body of the animal, and gave reactions with the Halphen reagent, indicating from 0.5 per cent. to 15 per cent. of cottonseed oil. The unsaponifiable residue was examined microscopically, and the acetate prepared, and its melting-point determined.

The method used for estimation of cholesterol was that suggested by Bömer,[3] and is as follows: Saponify 100 grams of the fat with 200 cc. alcoholic potash (200 grams KOH to 1 liter of 70 volume per cent. alcohol), using a reflux condenser. Transfer the soap solution, while still warm, to a separatory funnel from 1.5 to 2 liters in capacity, and add 400 cc. of water. After cooling, add 800-1000 cc. of ether, and shake vigorousy for from two to three minutes. Then separate the ether layer, and transfer to a flask and distil the ether. The extraction of the soap solution is repeated four times with 200 cc. of ether, and the ether residues all united. These are treated with 20 cc. of the alcoholic potassium hydroxide solution, and heated for a few minutes; 40 cc. of water added, and extracted with ether. The ether solution is washed two or three times with 10 cc. of water, or until free from soap, then transferred to a crystallizing dish, and the ether allowed to

[1] This Journal, **26**, 837 (1904).
[2] *Z. f. Offent. Chem.*, **7**, 140-143, 1901.
[3] *Z. f. Nahr. u. Genuss*, **1**, 38, 1898.

evaporate spontaneously. The residue is dried, and then taken up with 95 volume per cent. alcohol, and allowed to crystallize slowly.

Cholesterol, under these conditions, forms a layer of crystals on the surface of the liquid, while phytosterol crystallizes throughout the solution. This difference in manner of crystallization is quite marked. Under the microscope, these two substances show their characteristic crystals, as seen in the accompanying plates.

After the crystals have been examined, the alcohol is evaporated, and the residue treated with acetic anhydride, as described by Bömer[1] in his phytosterol acetate test, as follows:

Add 2 to 3 cc. of acetic anhydride, heat to boiling, and evaporate off the excess of anhydride on a steam-bath. The residue is recrystallized from 95 per cent. alcohol several times, and the melting-point determined. Bömer claims to detect by this method 1 per cent. of added cottonseed oil. The author was able to detect 2 per cent. quite readily.

Before examining these lards, considerable work had been done with pure lard and beef tallow, and mixtures of these with cottonseed oil. In some of these mixtures, heated cottonseed oil was used. This oil had been heated for twenty to thirty mintues, at 260° C., until it no longer reacted with the Halphen reagent, but this heating had no effect on the phytosterol acetate test.

It was found that from 6 to 8 per cent. of cottonseed oil added to either lard or tallow affected the crystalline form of the cholesterol to such an extent as to be easily recognized, the peculiar telescopic crystals of mixtures of cholesterol and phytosterol being formed. With additions of 5 per cent., the telescopic crystals are not formed, but there is a decided change in the crystalline form, which is readily recognized. With less than 5 per cent. of added cottonseed oil, there is not enough change from the pure cholesterol crystals to be sure of detecting the mixture.

The phytosterol acetate test gives a means of detecting these smaller additions, although mixtures, ordinarily made, could be detected by a microscopic examination.

The addition of 5 per cent. of cottonseed oil to a lard raises the melting-point of the acetate from 114° (uncor.), which was the maximum obtained with pure lards, tallows, and with cholesterol prepared from gall-stones, to from 118° to 119° (uncor.), while

[1] *Z. f. Nahr. u. Genuss.*, **4**, 1070 (1901).

an addition of 2 per cent. of cottonseed oil was readily detected, as it gave a melting-point of 115.8° (uncor.).

The thermometer used in this work was graduated from 85° to 200°, and in making the determination of melting-point, was immersed in the glycerin bath up to 100° mark, so that only from 13° to 20° of the mercury column was out of the bath, and as this would make only a slight stem correction, no correction has been made in the results reported in this paper. The actual melting-points obtained are slightly lower than those reported by Bömer, but as the results are very uniformly lower than his, it is probably due to a difference in the end-point taken, and also to the stem correction which he applies.

The melting-point of the third crystallization was taken, for as a rule there was not enough to make a fourth crystallization.

In Table I are given the results obtained on a number of samples of known composition.

TABLE I.—PHYTOSTEROL EXAMINATION OF LARDS AND MIXTURES.

Description.	Manner of formation of crystals.	Microscopical appearance.	Melting-point. Third crystallization
Pure lard	Cholesterol.	Cholesterol.	113.0° C.
Pure lard	"	"	113.0° C.
Pure lard	"	"	114.0° C.
Cholesterol from gall stones	"	"	113.8° C.
Cholesterol from tallow	"	"	113.0° C.
Pure lard + 2 per cent. cottonseed oil	"	"	114.8° C.
Pure lard + 2 per cent. cottonseed oil	"	"	115.8° C.
Pure lard + 4 per cent. cottonseed oil	like mixed crystals	like slightly impure cholesterol	117.0° C.
Pure lard + 5 per cent. cottonseed oil	mixed crystals	mixed	118.2° C.
Pure lard + 5 per cent. cottonseed oil	mixed crystals	mixed	119.4° C.
Pure lard + 5 per cent. cottonseed oil	mixed crystals	mixed	119.6° C.
Pure lard + 5 per cent. cottonseed oil	mixed crystals	mixed	118.° C.
Pure lard + 8 per cent. cottonseed oil	like phytosterol	telescopic crystals	119.5° C.

From these results it may be seen that very small additions of cottonseed oil can be detected in this way.

In Table II are given the results obtained on 15 samples of lard obtained from Fulmer, all of which gave the Halphen test.

TABLE II.—PHYTOSTEROL EXAMINATION OF LARDS FROM COTTONSEED-MEAL-FED HOGS.

Food laboratory No.	Elton Fulmer's No.	Source of fat.	No. of animals in lot.	Total amount of cottonseed-meal eaten. Pounds.	Pounds of meal eaten per 100 pounds. Pounds.	Coloration with Halphen reagent. Per cent. cotton-seed oil.	Crystal formation.	Crystalline form.	Melting-point of third crystallization of the acetate. °C
11161	1214	Kidney	4	47.0	35.9	15.0	Cholesterol	Cholesterol	113.0
11171	1265	"	4	37.0	20.2	15.0	"	"	113.5
11164	1249	Back	3	48.0	24.0	11.0	"	"	Lost
11170	1257	"	6	27.3	34.1	9.0	"	"	112.0
11162	1242	Jowl	1	154.0	75.0	8.0	"	"	Lost
11165	1219	Kidney	5	98.0	44.8	8.0	"	"	114.0
11167	1194	"	6	91.0	65.5	8.0	"	"	113.4
11169	1191	"	6	27.3	34.1	7.5	"	"	113.0
11175	1200	Intestines	1	154.0	75.0	7.5	"	"	113.6
11166	1227	Jowl	2	115.0	53.5	5.5	"	"	Lost
11168	1268	Intestines	5	98.0	44.8	5.5	"	"	113.6
11173	1267	Back	4	16.6	7.3	4.0	"	"	113.5
11163	1413	Composite	8	40.0	44.0	3.0	"	"	Lost
11174	1221	Intestines	4	16.6	7.3	1.0	"	"	112.0
11172	1225	Back	1	7.7	1.8	0.6	"	"	113.8

The lards in Table II are arranged in the order of the amount of coloration given with Halphen reagent. This varies from No. 11161, which gives a coloration equal to 15 per cent. of cottonseed oil to No. 11172, which gives a coloration equal to 0.6 per cent. of cottonseed oil.

The formation of the crystals was, in every case, like those from pure lard and pure cholesterol. Microscopically, they all looked like pure cholesterol.

The melting-points of the acetate were in no case higher than those obtained on pure lard, that is, 114°, and in all but two, ranged between 113° and 114°. The lower melting-points obtained for two samples were undoubtedly due to slight impurities, which are hard to remove in such small quantities as are obtained.

The melting-point of the acetate obtained from sample No. 11161, which gave a Halphen test indicating 15 per cent. of cottonseed oil was 113.5°, while that of No. 11172, which gave a test indicating 0.6 per cent., was 113.8°, showing pure cholesterol in both cases. This method, therefore, will differentiate between lards which give the Halphen test, because of added cottonseed oil and lards which give the test because of the feeding.

The fact that cholesterol has always been found in lards, tallows and similar animal fats, is well known, and yet the animals from which these fats are derived are very largely fed on vegetable foods containing phytosterol, such as Indian corn, and linseed meal, and yet the phytosterol from these substances has never been found in the fat. By analogy, it would be expected that the phytosterol from cottonseed meal would not appear in the hog fat.

These considerations give added weight to the analytical results in Table II. The results of this work may be summed up in the following conclusions:

First, that lard from cottonseed-meal-fed hogs does not contain phytosterol, which confirms Solstein's work.

Second, that small amounts of added cottonseed oil can be detected in lard by this method, confirming Bömer's work.

Third, that heated cottonseed oil, which does not give the Halphen test, can be detected by this method.

Plate I shows the cholesterol crystals obtained from a sample of lard rendered in the laboratory.

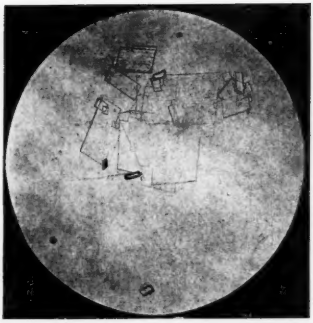

Plate I.

Plate II.

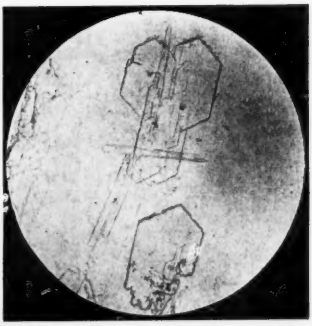

Plate III.

Plate IV.

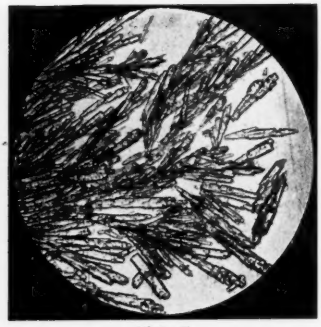

Plate V.

Plate VI.

Plate II shows the cholesterol crystals from one of Fulmer's lards, which gave a Halphen reaction about as strong as if 10 per cent. of cottonseed oil had been present.

Plate III shows phytosterol crystals from cottonseed oil.

Plate IV shows crystals from a mixture of 75 per cent. cholesterol, and 25 per cent. phytosterol with the characteristic telescopic effect produced by mixtures.

Plate V shows crystals from lard containing 10 per cent. of added cottonseed oil.

Plate VI shows crystals from lard containing 10 per cent. of heated cottonseed oil. This lard did not give the Halphen test, but the presence of cottonseed oil is at once detected in the form of the crystals.

The photomicrographs of the crystals were made by Mr. B. J. Howard, of the Bureau of Chemistry.

NOTE.—After this article had been submitted for publication, another paper on the same subject, by Emmett and Grindley, appeared in this Journal.[1] Their conclusions being so entirely opposed to those of Bömer, Solstein and others, as well as to the results of this paper, the author has felt compelled to call attention to what appears to him the weakness in their proof. They state that the crystals of the unsaponifiable residue, which they obtained from the lard from hogs fed on cottonseed oil appeared like phytosterol. Granting this to be true, there must have been a very large percentage of the phytosterol present, for as will be seen from Plate IV, 25 per cent. of phytosterol and 75 per cent. of cholesterol still give the peculiar telescopic form of crystal. In fact, the author has found that before crystals are obtained, which cannot be distinguished from phytosterol, at least 50 per cent. of phytosterol must be present. With such an amount, as must have been present in order to give the phytosterol-shaped crystals, it would be extremely easy to detect its presence by the melting-point of the acetate, which would be about 123 to 125° C., instead of 114° C., the melting-point of pure cholesterol acetate. This, the authors say they were unable to do.

The author working on a large number of lards from all parts of the body, some of which gave very marked reactions with the

[1] **27**, 263 (1905).

Halphen test, was unable to detect phytosterol, although the presence of phytosterol was easily recognized when only 2 to 3 per cent. of cottonseed oil was added. The crystals from these lards were all true cholesterol forms, and gave the correct melting-point when treated with acetic anhydride and purified.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 104.]

A STUDY OF METHODS FOR THE DETERMINATION OF FORMALDEHYDE.

BY R. H. WILLIAMS.

Received March 9, 1905.

THE work herein described consists of a comparison and criticism of the four methods most generally recommended for the determination of formaldehyde—Legler method,[1] hydrogen peroxide method,[2] iodimetric method,[3] and potassium cyanide method.[4] Having no means of obtaining formaldehyde in a pure, anhydrous state it became necessary to study the accuracy of these methods by indirect and comparative, rather than by direct and absolute tests. First, the conditions usually given for these methods were followed, and then such modifications tried as were believed to give increased accuracy or greater rapidity, the ultimate object being to determine, if possible, the best conditions for each method, and then to form a judgment as to their comparative merit.

Legler Method.—The conditions maintained were essentially those given by Smith.[5] Thirty determinations of formaldehyde were made under these conditions variously modified, and the results obtained established the following facts: That the best end point is obtained when a rather dilute solution of formaldehyde is taken, and N/5 reagents are used. That it is best to carry on the reaction in small flasks or bottles, thus minimizing the free space over the reacting liquids. That, after standing twenty-four hours, the maximum absorption takes place when the excess of ammonia is 1 cc. or more, and when the concentration of the

[1] Legler: *Ber. chem. Ges.*, **16**, 1333.
[2] Blank and Finkenbeiner: *Ibid.*, **31**, 2979.
[3] Romijn: *Z. anal. Chem.*, **36**, 18-24.
[4] *Ibid.*
[5] This Journal, **25**, 1028.

same is not less than N/8. The results from six additional determinations, made in a solution of formaldehyde of approximately 2 per cent., and calculated on the original solution, are as follows:

	Per cent.	Per cent.	Per cent.
After standing 24 hours.....	34.76	34.84	34.88
" " 48 "	34.96	34.82	.....
" " 9 days.....	34.95	.....	.....

Six determinations were made, using 2 to 3 grams of the original solution (Kahlbaum's formaldehyde) in each case. The results are: 34.75, 35.06, 34.99, 35.02, 34.90, 34.63 per cent.

While the results are in accord with those previously obtained, the end-point was not as satisfactory as when the more dliute solution was used, which accounts for the greater variation in the results.

The best conditions for this method, are as follows: Weigh into a 250 cc. glass stoppered flask, 15 grams of the commercial formalin, and dilute to the mark. This solution will contain approximately 2 per cent. of formaldehyde. After determining its acidity in terms of the standard ammonia, place 10 cc. in a small bottle or flask, provided with a well-fitting stopper, and add 40 to 50 cc. of N/5 ammonia solution. Allow to stand for twenty-four hours, then titrate the excess of ammonia with N/5 acid, sulphuric or hydrochloric, using not more than 2 drops of 0.1 per cent. rosolic acid solution as indicator.

Hydrogen Peroxide Method.—The first determinations were made under the conditions given by Smith[1] with these modifications,—about 2 grams of Kahlbaum's formaldehyde were taken, while the concentrations of the acid and alkaline solutions were respectively normal and 1½ normal. Low results were obtained, due, no doubt, to the rather unusual temperature conditions, and the less concentrated alkaline reagent. The temperature of the room in which this work was done rarely exceeded 15° C., and under these conditions, the time usually allowed the reaction, (ten to fifteen minutes), was not sufficient to insure complete oxidation.

Four additional determinations were made, and in each case, the flasks were well shaken several times, and allowed to stand until the escape of gas practically ceased. The time required was

[1] *Loc. cit.*

about one hour. The results are: 35.82, 35.92, 35.74, 35.78 per cent.

The best conditions for this method are as follows: Weigh portions of 2 grams each of formalin in 250 cc. Erlenmeyer glass-stoppered flasks, and add to each 30-40 cc. standard sodium hydroxide, 1 to 2 normal, preferably normal. Add cautiously from a pipette, 50 cc. of hydrogen peroxide solution. Shake at intervals of three to five mintues for fifteen minutes to one hour, depending upon temperature and concentration of reagents, then titrate the excess of sodium hydroxide with sulphuric acid, using 8 to 12 drops of litmus as indicator. The acidity of the hydrogen peroxide and formalin must be determined, and the figures obtained enter into the calculation.

Iodimetric Method.—The conditions as given by Smith were followed. The results of six determinations are: 35.57, 35.44, 35.71, 35.70, 35.64, 35.70 per cent.

Six additional determinations were made to test the influence on the results of different amounts of iodine in excess. The results are:

5 cc. I in excess. Per cent.	25 cc. I in excess. Per cent.	35 cc. I in excess. Per cent.
35.49	35.51	35.53
35.67	35.69	35.77

Potassium Cyanide Method.—The conditions followed were essentially those given by Romijn. The only modifications were such as affected the volume and concentration of some of the reagents.

Place 15 cc. N/10 silver nitrate in a 100 cc. flask and acidify with 8 to 10 drops of 50 per cent. nitric acid. Add 10 cc. of a solution of potassium cyanide approximately N/10, dilute to the mark, mix thoroughly, and filter. Titrate 50 cc. of the filtrate with N/40 ammonium sulphocyanate for excess of silver nitrate, using 5 cc. of a saturated solution of ferric alum as indicator. From the data thus obtained, the ratio between the potassium cyanide and silver nitrate solutions can be calculated. Another portion of the N/10 silver solution, 10 to 20 cc., is acidified as before, and then added to 30 to 40 cc. of the potassium cyanide solution, which has previously been treated with 10 cc. of the formaldehyde solution (about 1 per cent.). After shaking thoroughly, the excess of the silver nitrate solution is determined in an aliquot part of

the filtrate, as before. The percentage of formaldehyde may be found from the following formula:

$$\frac{\text{cc. } AgNO_3 \text{ [Equiv. to cc. of KCN absorbed]} \times 0.003 \times 100}{\text{weight of } CH_2O \text{ taken}} = \%$$

Six determinations were made, yielding the following percentages: 35.15, 35.06, 35.20, 35.01, 35.21, 35.07.

Discussion of Results.—From a review of the percentages thus far obtained, it was observed that the two oxidation methods gave closely agreeing results, and the same was true of the condensation methods, yet the former gave results a per cent. higher than the latter. It was thought that the variation might be due either to the presence of some impurity capable of oxidation, or to a polymerized form of formaldehyde, which affected unequally the two types of methods. As Kahlbaum's formaldehyde had been used exclusively in these determinations, it was thought that a set of estimations of formaldehyde made in commercial formalin, and another in paraformaldehyde, would clear up the point in question. A sample, largely paraformaldehyde, was obtained from commercial formalin, being the residual liquid after distilling off two-thirds of the original volume.

The averages of from two to ten determinations are given below.

	Methods.			
Formaldehyde used.	Legler.	H_2O_2.	Iodimetric.	KCN.
Kahlbaum's	34.87	35.82	35.66	35.12
Commercial formalin	35.06	36.14	36.15	35.24
Largely paraformaldehyde	49.45	51.00	51.24	49.76

The discrepancies between the results obtained from the oxidation and condensation methods are the same in character, whatever the nature of the sample taken. The extent of the discrepancy is greatest in the case of the largely polymerized form, which is easily explained by the increased concentration. Since the variation cannot be explained by the presence of either impurities or paraformaldehyde, it was thought that in the case of the Legler method, the low results might be due to the instability of hexamethylenetetramine in the presence of a strong acid. Should compounds of an alkaline nature arise in this way, low results would be inevitable.

Eight determinations were made, acetic acid being used to determine the excess of ammonia in four of these, and sulphuric acid in the others. The results are:

With acetic acid.		With sulphuric acid.	
34.99	34.89	34.79	34.86
34.78	34.95	34.72	34.91

It should be stated that, in all this work where the excess of ammonia was titrated with acid, the neutral point was taken to be that at which the last trace of pink disappeared. When such small quantities of rosolic acid are used, the liquid is practically colorless at this point. Had the first color change been taken as the end-point, results more nearly in accord with those of the oxidation methods would have been obtained.

The applicability of these methods to the determination of formaldehyde in the presence of other substances was studied. Tests were made with ethyl alcohol, paraldehyde, acetaldehyde, acetone and methyl alcohol, and carried out in the following manner.[1] Three drops of the substance, whose influence was to be tested, were added, with the prescribed amount of formaldehyde in each case, and the latter determined according to the conditions given. Where the substance added had no influence, the result is given as "normal," otherwise the actual percentage is given.

		Substance added.				
Method.	Formaldehyde. Per cent.	Ethyl alcohol.	Paral-dehyde.	Acet-aldehyde.	Acetone.	Methyl alcohol.
Legler.....	34.87	Normal	Normal	47.8	Normal	Normal
H_2O_2.....	35.82	"	"	38.6	"	"
Iodimetric	35.66	36.4	36.5	39.6	50+	36.49
KCN.....	35.12	Normal	Normal	35.30	Normal	Normal

CONCLUSIONS.

(1) The iodimetric method is rapid and accurate; and preferable for pure, dilute solutions.

(2) The hydrogen peroxide method is the most satisfactory for strong, impure solutions. The time necessary for a complete oxidation is widely variable, depending upon concentration and temperature.

(3) The potassium cyanide method is recommended for dilute, impure solutions. The results are lower than those obtained by the oxidation methods.

(4) The end-point in the Legler method is not satisfactory,

[1] For previous experiments on the influence of some of these substances, see Romijn: *Z. anal. Chem.*, **36**, 18-24. Blank and Finkenbeiner: *Ber. chem. Ges.*, **31**, 2979. L. Peska: *Chem. Ztg.*, **25**, 743.

which fact, as well as the low results, must be attributed to causes other than the influence of strong acids on hexamethylenetetramine.

(5) Paraformaldehyde, when present, counts as formaldehyde.

(6) The discrepancy in the results obtained by the two different types of methods is due to conditions inherent in the methods themselves—not to the presence of impurities or to a polymerized form of formaldehyde. Apparently, either the condensation reactions are not complete, or a small part of the formic acid, produced by the oxidation reactions is oxidized farther, giving high results.

QUANTITATIVE LABORATORY,
March 1, 1905.

A COLORIMETRIC METHOD FOR THE DETECTION AND ESTIMATION OF FORMALDEHYDE.

BY FREDERIC BONNET, JR.

Received February 23, 1905.

IT HAS been pointed out[1] that certain alkaloids give very characteristic color reactions with formaldehyde. A closer investigation of this subject has shown that these reactions can be applied not only to the qualitative detection, but also, in some cases, to the quantitative estimation of formaldehyde.

If a substance containing formaldehyde is placed in an evaporating dish and 1 cc. of a freshly prepared sulphuric acid solution of morphine in a watch-glass is floated or placed upon it, the morphine solution becomes more or less colored, varying from pink to dark blue, according to the amount of formaldehyde present. The coloration is due to the vapor of the formaldehyde, which reacts with the morphine. By this method so small an amount as 4 parts of formaldehyde in 1,000,000 can be detected.

The morphine sulphate solution is made by dissolving 0.35 gram of white crystalline morphine sulphate in 100 cc. of cold, strong, chemically pure sulphuric acid (sp. gr. 1.84). Unfortunately, this solution does not keep any great length of time, as the sulphuric acid slowly decomposes the morphine, even at ordinary temperatures.[2] The following tests were made, therefore, with fresh solutions.

[1] Grünhut: *Z. anal. Chem.*, **39**, 329 (1900).

[2] Allen's "Commercial Organic Analysis," **8**, 314 (1892).

MILK.

About 60 cc. of milk, containing a known amount of formaldehyde, were placed in a 3-inch evaporating dish; and 1 cc. of the morphine solution was floated upon the surface by means of a 1 inch watch-glass. The dish was then immediately covered with a 4 x 5 inch glass plate. The results are given below.

TABLE I.—TEMPERATURE 20° C.

No.	Containing CH_2O.	Remarks.
1	Pure milk	No coloration after 3 hours.
2	4 : 100	Coloration appeared in a few minutes, which soon turned black.
3	4 : 1,000	Coloration appeared in a few minutes. Upon standing it also turned black.
4	8 : 10,000	Good ring colorating after about 8 minutes.
5	4 : 10,000	" " " " " 15 "
6	8 : 100,000	Fairly good ring coloration in about 45 minutes.
7	4 : 100,000	" " " " " 1 hour.
8	8 : 1,000,000	Slight coloration throughout, in about 1¾ hours.
9	4 : 1,000,000	" " " " " 2½ "

In the following experiment an attempt was made to determine the time of formation of the first definite ring or color:

TABLE II.—TEMPERATURE 12° C.

No.	Containing CH_2O.	Remarks.	
1	Pure milk	No coloration after 9 hours.	
2	4 : 100	Definite ring in about 4 min.	Black in 15 min.
3	8 : 1,000	" " " " 5 "	
4	4 : 1,000	" " " " 6½ "	Blue black in 30 minutes.
5	8 : 10,000	" " " " 10 "	
6	4 : 10,000	" " " " 16 "	Pink then brown.
7	8 : 100,000	" " " " 50 "	
8	4 : 100,000	" color in about 2 hours.	
9	8 : 1,000,000	Slight " " " 4 "	
10	4 : 1,000,000	Practically no color after 9 hours.	

Comparison of the two tables shows that the temperature is an important factor when testing for very small amounts of formaldehyde. About 20° was found to be the most convenient and serviceable temperature for making the test.

To determine whether formaldehyde could still be detected by the morphine reaction, in milk which had undergone decomposition, the solutions of Table I were allowed to stand one week at

room temperature (±18° C.) in tightly stoppered bottles. At the end of this time they were again tested.

TABLE III.—TEMPERATURE 20° C.

No.	Containing CH_2O.	Condition of milk.	Remarks.
1	None	Spoiled after about 12 hrs.	No coloration after 4 hrs
2	4 : 100	Good	Coloration in a few min.
3	4 : 1,000	Good	Coloration in a few min.
4	8 : 10,000	Good	Good ring coloration.
5	4 : 10,000	Good	" " "
6	8 : 100,000	Spoiled on 6th day.	Fairly good ring coloration.
7	4 : 100,000	Spoiled on 3rd day.	Fairly good ring coloration.
8	8 : 1,000,000	Spoiled on 2nd day	Slight coloration
9	4 : 1,000,000	Spoiled after about 12 hrs.	Practically no coloration.

The results in Table III show that the morphine test is applicable even when the milk has undergone decomposition.

BUTTER.

The morphine test was also tried with butter. Fresh butter, free from preservatives, was worked up for fifteen minutes in an aqueous solution containing 4 parts of formaldehyde to 100 of water. After pouring off the solution the butter was rolled into a ball. Similar sized lumps of butter were treated in the same way with solutions containing 4 : 1,000 and 4 : 10,000. The balls, allowed to air-dry uncovered for eighteen hours, were flattened on the bottoms of 3-inch evaporating dishes and the tests made as with the milk. In this case small porcelain crucibles were used for the morphine solution.

TABLE IV.—TEMPERATURE 18° C.

No.	Solutions containing CH_2O.	Remarks.
1	Pure Butter	No coloration.
2	4 : 100	Coloration in a few min.
3	4 : 1,000	" " " "
4	4 : 10,000	" " 15 min.

The above butter, after standing in a warm place for one week, gave the following results:

TABLE V.—TEMPERATURE 18°.

No.	Solutions containing CH_2O.	Condition of butter.	Remarks.
1	None	Decomposed	No color
2	4 : 100	Good	Coloration in few min.
3	4 : 1,000	Good	Coloration strong
4	4 : 10,000	Slightly decomposed	Coloration

Since the test depends solely upon the composition of the vapor above a liquid or moist surface, only those substances can interfere which have appreciable vapor pressures and which react with the morphine solution.

Salicylic acid, benzoic acid and hydrogen peroxide, the common preservatives of this nature were tested and gave no reaction. Various other substances were tested in this connection from time to time and very few gave any color reactions whatever. Thus, acetone, ethyl ether, ethyl alcohol, chloralhydrate, chloroform, formic acid, furfural, carbon bisulphide, gave no reaction, while methyl alcohol, acetaldehyde and acrolein, in strong pungent solutions, gave pale brownish and benzaldehyde, and fusel oil light yellow colorations, all of which are very different from the characteristic formaldehyde test.

QUANTITATIVE ESTIMATION.

Experiments to determine whether the foregoing test could be applied quantitatively were made as follows:

A standard solution of milk was made by dissolving 11 cc. of a Kahlbaum solution containing 34 per cent. by weight[1] of formaldehyde in 100 cc. of milk, giving a solution of 4 : 100. From this, solutions containing 8 : 1,000, 4 : 1,000, 8 : 10,000, 4 : 10,000, 8 : 100,000, 4 : 100,000, 8 : 1,000,000, and 4 : 1,000,000 were made by adding the required amount of milk.

Samples of milk containing varying amounts of formaldehyde were then prepared, the amount in each being unknown, for the the time being, to the experimenter. Sixty cc. of each of these samples were placed in evaporating dishes and tested as in the qualitative trials. The approximate time of the first ring or color formation gave an idea (as is shown by Table II) of the amount of formaldehyde present. Knowing approximately the amount of formaldehyde in solution, fresh portions of the unknown milk were compared with the corresponding standard solutions, care being taken that the tests were started at the same time and were made under like conditions.

In each of the above prepared unknown samples the amount of formaldehyde found was essentially the same as that which had been put into the solution. Over a range extending from 8 : 1,000 to 8 : 1,000,000, solutions containing the same amounts of formal-

[1] *Z. anal. Chem.*, **44**, 13 (1905); also. This Journal, **25**, 1028 (1903).

dehyde gave the same characteristic coloration in the same period of time. It is necessary for accurate work that equal amounts of the unknown and known solutions be taken, and that the amounts of the morphine solution used should be the same; also the evaporating dishes and the watch-glasses should be alike both in size and shape.

SUMMARY.

This method gives not only a simple means of detecting formaldehyde, but in the case of liquids allows of its estimation. It is applicable when the formaldehyde is present with a great variety of substances and can be adapted with almost equal facility to both liquid and solid products.

In conclusion I wish to thank Dr. L. W. Andrews for his kind suggestions.

WORCESTER POLYTECHNIC INSTITUTE,
February 16, 1905.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 105.]

THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE ANALYTICAL CONSTANTS OF FATTY OILS.

(SECOND PAPER.)

BY H. C. SHERMAN AND M. J. FALK.

Received March 6, 1905.

IT HAS been shown[1] that non-drying and semi-drying oils, on exposure to air, undergo changes similar to those which take place when the corresponding fatty acids are treated with potassium permanganate in alkaline solution, oleic acid being apparently converted into dioxystearic, and linoleic into sativic acid. The "oxidation," therefore, appears to result mainly in the addition of hydroxyl groups, two of these groups taking the place which, in the determination of the iodine number, would have been taken by two halogen atoms. If, as stated by Ballantyne,[2] atmospheric oxidation causes no change in the volume of the oil, the increase in specific gravity and the decrease in iodine absorbing power are to each other as the weight of the hydroxyl group is to that

[1] This Journal, **25**, 711 (1903).
[2] *J. Soc. Chem. Ind.*, **10**, 29 (1891).

of the iodine atom. Calculating both of these changes on the basis of the original weight of oil the relation would be:

Percentage increase in specific gravity : Decrease in iodine number : : OH : I or as 1 : 7.46.

This calculation was applied to "exposed" samples of olive, lard, cottonseed, maize and poppy-seed oils, and has been used successfully by students in identifying "unknown" oils, which had been so altered by exposure as to give iodine numbers considerably below the normal limits. Additional experiments have recently been made to determine whether the proportion applies with equal accuracy, when the oxidation is allowed to go farther. Determinations of acidity and of index of refraction have also been made in some cases.

The principal results are shown in the following table:

INFLUENCE OF EXPOSURE UPON SOME OF THE ANALYTICAL "CONSTANTS."

Description of oil.	Specific gravity $\frac{15.5^\circ}{15.5}$ (D)	Iodine number.	Free acid calculated as oleic. Per cent.	Index of refraction at 15.5° (N)	Specific refractive power $\left(\frac{N-1}{D}\right)$
Neatsfoot, fresh	0.9160	60.9	....	1.4685	0.5115
" after exposure	0.9285	51.2	10.67	1.4692	0.5053
Lard oil, I, fresh[1]	0.924	69.3	....	.....	.....
" after exposure	0.943	54.6	9.98	.....	.....
Lard oil, II, fresh	0.917	73.3	0.90	1.4697	0.5122
" after exposure	0.943	56.2	4.96	1.4724	0.5010
Sperm, fresh	0.886	78.5	....	.....	.....
" after exposure	0.926	48.9	5.85	1.4724	0.5102
Olive, fresh	0.9165	83.8	2.65	1.4712	0.5141
" after exposure	0.924	77.3	....	1.4722	0.5100
Almond, fresh	0.919	97.0	5.92	.....	.....
" after exposure	0.9355	83.9	7.84	.....	.....
Cottonseed, I, fresh	0.920	102.8	0.14	.....	.....
" after exposure	0.938	89.9	2.96	.....	.....
Cottonseed, II, fresh	0.923	105.2	....	1.4737	0.5132
" after exposure	0.939	90.2	....	1.4779	0.5090
Maize, I, fresh	0.924	117.2	....	.....	.....
" after exposure	0.939	105.7	....	.....	.....

[1] This sample may have begun to change before the first examination, as the specific gravity is abnormally high.

Description of oil.	Specific gravity $\frac{15.5°}{15.5}$ (D)	Iodine number.	Free acid calculated as oleic. Per cent.	Index of refraction at 15.5° (N)	Specific refractive power $\left(\frac{N-1}{D}\right)$
Maize, II, fresh[1]	0.9213	118.6	1.13	1.4764	0.5171
" after exposure	0.990	63.4	12.52	1.4779	0.4827
Linseed, I, fresh	0.934	177.1	1.26	1.4835	0.5177
" after 1st exposure	0.954	148.1	2.05	.....	.....
" " 2nd "	0.969	136.9	....	1.4886	0.5042
Linseed, II, fresh	0.934	180.2	1.33	.....	.....
" after 1st exposure	0.942	165.8	2.23	.....	.....
" " 2nd "	0.966	140.1	4.48	.....	.....
Linseed, III, fresh	0.934	184.8	....	.....	.....
" after exposure	0.951	160.0	....	.....	.....
Linseed, IV, fresh	0.9345	186.3	....	.....	.....
" after exposure	0.948	159.1	....	.....	.....

It will be seen that, in the case of every oil examined, the index of refraction had increased at the same time with the specific gravity, but not to the same extent, so that the specific refractive power calculated by Landolt's formula $\left(\frac{N-1}{D}\right)$ is in each case considerably diminished.[2]

In testing oils of unknown history, this fact will be found useful. An oil having low iodine number and specific refractive power, with high specific gravity, index of refraction and Maumené number may be considered as having undergone partial oxidation, as the result either of exposure or of "blowing."

When the iodine numbers of the oxidized ("exposed") oils are corrected on the basis of the change in specific gravity, according to the theory, as explained above, the results obtained are all within the normal variations of oils of the same species;[3] but

[1] This was one of the samples used by Vulté and Gibson in their investigation of maize oil (this Journal, **22**, 453 (1900); **23**, 1 (1901). Professor Vulté having kindly furnished one of us a small portion of the sample at that time, it was kept in a partially filled bottle for five years. When examined at the end of this time the oil had become so viscous as to be barely fluid at 15.5° so that the specific gravity could not be determined with certainty to the third decimal place.

[2] Compare the results obtained in the examination of a rancid butter fat by Browne, whose paper (this Journal, 1899, **21**, 975-994) includes a review of the earlier work.

[3] The discussion in the text applies only to non-drying and semi-drying oils. The results of our experiments on partially oxidized linseed oils are included in the table for comparison and reference although they are not sufficiently uniform to suggest a factor for correcting the iodine numbers of such oils.

the agreement with the original iodine numbers is not always as close as the accuracy of the analytical methods would allow. Probably a simplified method of correction will be found fully as accurate and more convenient. The following is suggested:

To find the original iodine number of a semi-drying or non-drying oil, which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity $\left(\text{taken at } \frac{15.5^\circ}{15.5^\circ}\right)$

The last column in the following table shows the results obtained by correcting according to this rule.

CORRECTION OF IODINE NUMBERS OF OXIDIZED OILS.

No.	Description.	In fresh condition.	Iodine number after exposure. Without correction.	Corrected according to theory.	Corrected by simplified method.
1.	Neatsfoot oil	60.9	51.2	61.9	61.2
2.	Lard oil, I	69.3	54.6	71.0	69.8
3.	Lard oil, II	73.3	56.2	78.8	77.0
4.	Sperm oil	78.5	48.9	84.7	80.9
5.	Olive oil	83.8	77.3	83.8	83.3
6.	Almond oil	97.0	83.9	97.8	97.1
7.	Cottonseed oil, I	102.8	89.9	106.2	104.3
8.	Cottonseed oil, II,	105.2	90.2	104.7	103.0
9.	Maize oil, I,	117.2	105.7	119.4	117.7
10.	Maize oil, II	118.6	63.4	124.1	118.4
	Average	90.86	.....	93.24	91.27
	Average omitting (No. 3)	92.81	.....	94.84	92.86

It will be seen that the simple rule suggested above, gives results sufficiently accurate for all ordinary purposes, even when applied to oils which had lost from 15 to 45 per cent. of their original iodine absorbing power. It is applicable to sperm oil as well as to fatty oils.

When the original specific gravity is not known, the calculation must be based on the average specific gravity for the species of oil under examination. Any error involved in this assumption will be too small to affect seriously the interpretation of the results.

QUANTITATIVE LABORATORY,
March 1, 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

SOME EXPERIMENTS ON THE FUEL VALUE OF BITUMINOUS COAL ASHES.

BY HENRY FAY AND F. W. SNOW.

Received February 25, 1905.

DURING the winter of 1902-3, when the scarcity of coal was so great, it was considered desirable to know the exact amount of unburned coal, which was being thrown away in our ordinary soft coal ashes. From some experiments carried out, under the direction of and reported upon, by the late Col. Waring,[1] the amount of unburned coal seemed to him large enough to warrant the city in recovering this coal, and he also recommended various uses for the ashes. By means of a specially constructed small boiler, built on the order of a Rumford calorimeter, measurements were made of the unburned coal in the ash. The amount of waste coal in ashes examined varied from 20 per cent. to 40 per cent. by weight. If the ashes from the tenement-house district be included, the average would fall to about 20 per cent. It is further estimated, that on this average there would be lost about 125,000 tons of coal for every 1,000,000 cubic yards of ashes. These numbers seemed to show such an appalling loss that it seemed highly desirable to subject the question to further experiment. As the method for determining these values was not strictly accurate, it was decided to repeat some of this work in such a way that the personal element was reduced to a minimum, and to express the results in terms of standard values.

In order to test the fuel value, ashes were obtained from four sources; *viz.*, the Rogers Building heating plant of the Massachusetts Institute of Technology, the Edison Electric Light Co., the Hotel Berkeley, and from a large packing house in which was used a mechanical stoker. These four samples will be referred to as A, B, C and D respectively. Starting with barrel lots, each one was carefully weighed, and was then subjected to a screening process, in order to classify the material into coarse, medium and fine ashes, so that in case there was enough coal in any one of these products to warrant its recovery, a commercial extraction might

[1] Report of the Department of Street Cleaning of the City of New York, 1895-97.

be developed. These separate lots were weighed, and then sampled by coning and quartering. The final sample in each lot was then crushed and powdered, and from this material the calorific value was obtained. In this way the calorific value of samples from the coarse, medium, and fine ashes was obtained, and represented a true average of the whole.

All determinations were made in a Mahler bomb with all the precautions necessary for accurate work, with the exception, that no corrections were made for sulphur compounds, which may have been in the ash, nor in the coal, which it was necessary, in some cases, to add. The values, which are given, therefore, are not, strictly speaking, absolute values. The corrections, which would be necessary, however, would be exceedingly small, and the values given are not far from the actual truth. As all experiments were carried out under the same conditions, the values are strictly relative. Attempts were made at first to burn the ash direct, but this was successful with the richest products only. In the poorer products there was some combustion, but the heat developed was sufficient to soften the slag, which formed a glassy mass, protecting the unburned part from further action of the oxygen. On account of this difficulty, it was found necessary, in each case, to add a weighed quantity of standard coal, and to burn this with the ash. A blank determination of the calorific value of the coal was made before each determination of the ash, and knowing the number of calories contained in the coal, the difference represented the number of calories in the ash.

The following table shows the results obtained in the screen analysis, and the value in calories of the various products. It will be noticed that the percentages given are obtained from comparison with a coal giving 8,500 calories, instead of the actual fuel value of the coal from which the ash was obtained. This was considered desirable, since it was necessary, in some cases, to add some such coal to the ash, in order to make a perfect combustion.

Sample.	Screen analysis.	Weight in kilos.	Percentage weight.	Total calories.	Calories per gram.	Percentage of unburned coal compared with a coal giving 8500 calories.
	On 1-inch mesh	16.2	49.85	1320.3	81.5	0.96
A	Through 1 on 2	9.4	28.92	2596.3	276.2	3.25
	" 2	6.6	20.31	1840.1	278.8	3.28
	Loss	0.3	0.92	———	.....	.....
	On 2-inch mesh	20.5	44.4	45811.5	2234.7	26.29
B	Through 2 on 4	14.1	30.5	24648.2	1748.1	20.51
	" 4	11.5	24.9	10574.2	919.5	10.82
	Loss	0.1	0.2	.....	.....	.....
	On 1-inch mesh	4.8	11.4	2674.1	557.1	6.55
C	Through 1, on 2	8.1	18.9	4770.1	588.9	6.93
	" 2, on 4	8.6	20.0	4767.8	554.4	6.52
	" 4	20.8	48.6	.....	.....	.....
	Loss	0.5	1.1	.....	.....	.....
	On 2-inch mesh	33.0	23.86	35805.0	1085.0	12.76
D	On 4-inch mesh	39.7	28.71	83688.0	2108.0	24.80
	Through 4	65.4	47.28	101370.0	1550.0	18.24
	Loss	....	0.15	.....	.....	.....

It will be seen from an inspection of the table, that in two of the samples, the value in coal approaches the results reported upon by Col. Waring, and in those two it is not uniformly distributed in the different sizes. In sample B the highest values are obtained with 26.29 per cent. in the coarse material, which was composed largely of black clinker, holding mechanically enclosed coke and coal. This appearance was also characteristic of the smaller sizes of this sample, indicating a fairly poor coal to start with, and considerable neglect on the part of the fireman. While the amount of unburned coal actually present seems high, judging by the figures which were obtained, it does not seem to be in a form which would make it worth while to save. Instead of existing in the form of separate pieces of coal, most of it was in the form of coke, adhering firmly to, and partially fused into the clinker. A more careful fireman certainly could have decreased this value very considerably. In sample D, the material on the 2-inch mesh also shows a high value. This is, however, to

be traced directly to the character of the slag, which is formed on heating. The clinker melts at a low temperature enclosing coal and coke, and falls through the grate in the form of round pellets of slag. In this material there is apparently no coal, and judging alone from the appearance, it would be pronounced free from it, but on breaking open the shell of a pellet, there is invariably some coal enclosed. This material would not appear to have much value, notwithstanding the high percentage of unburned coal found.

Sample A represents the average run of ash from a good grade of Pocahontas coal. It was taken from the middle of three grates. The ash from the top grate consists only of very coarse clinker, while that from the lower grate contains only very fine ash, both, judging from the appearance only, apparently free from coal.

The material used in this work represents only a very few of the large types of plants, and consequently, it would be unwise to draw from the results any definite conclusions. It is believed, however, that the results represent something near the average. In the cheap tenement districts, there would, undoubtedly, be found very little coal, because of the scrutiny with which the ash is sifted and picked over. On the other hand, from the private residence, and apartment-house district, where the waste is larger, and where there is little or no attempt to work over the ashes, the average would probably be higher than the results reported here.

The average per cent. of unburned coal for each sample is, respectively, 2.49, 19.20, 6.66 and 18.60, and the average for the four only 11.98. This is very considerably lower than the average values reported upon by Col. Waring, and it is believed that the expense of collecting and working the material of this kind would exceed the profit on the recovered product, unless the recovery was done in connection with some scheme for the utilization of the clinker and fine ash.

This conclusion, however, should be accepted only as tentative, as it would be necessary to use a much larger series of samples, not only of bituminous, but also anthracite coals for a final decision of the question.

BOSTON, February 23, 1905.

NOTES.

The Occurrence of Benzoic Acid Naturally in Cranberries.—The chemists of the various State Dairy and Food Commissions have upon numerous occasions, published reports of preservatives found in certain food products which the manufacturer has denied placing in them. This fact has been brought before the writer upon several occasions, especially in regard to cranberry sauce, which it has been found does not require the use of a preservative in any instance. In all reports at the writer's command where a cranberry sauce has been examined, benzoic acid has been reported as having been used as a preservative. Knowing of Oscar Loew's report[1] on the occurrence of a small amount of benzoic acid naturally in cranberries, and supported by the strong denial of the preservative's addition by the manufacturer, the writer thought that benzoic acid might have occurred in larger quantities than supposed in this fruit.

With this end in view, samples of cranberries were purchased in the open markets of Allegheny and Pittsburg, Pa., and tested for benzoates. All of these contained benzoic acid in comparatively large amounts. The crystals produced on sublimation were sufficient evidence for any chemist to pronounce the samples preserved by the addition of benzoic acid. In order to be sure of the purity of the samples to be tested in verification of the above results several cranberry growers from different sections of the Northeast were written to, asking for samples of the berries and vines from the time the blossom appeared until the berries were fully ripe. Samples were received from growers in New Jersey, Massachusetts and Wisconsin. The first berries received were very small and green, but contained a faint trace of benzoic acid. The larger and older the berries became, the more benzoic acid was found to be present until a maximum was reached, when the berries became overripe and a very dark red. This shows that the acid forms during the process of ripening of the berry and increases up to full ripeness. The largest amount found was approximated at 1 part of the acid to 2,000 parts of the cranberries. This was determined by comparison with that produced from fruits containing a known added amount of benzoic acid. This amount is

[1] *J. prakt. Chem.* [2], **19**, 312.

equal to that used in the preservation of most perishable foods, and in some cases is even larger than the amount necessary to preserve. The vines were tested at intervals during the cranberry season, but not even a trace of benzoic acid could be found.

The writer called the attention of Dr. W. D. Bigelow, of the United States Department of Agriculture, to the exceptionally large amount of benzoic acid naturally in cranberries, who immediately began a thorough investigation of this matter. We worked entirely independently of each other all summer and fall, and as far as I have been able to ascertain, our results have agreed in nearly every detail.

G. F. MASON.

DEPARTMENT OF CHEMICAL RESEARCH,
H. J. HEINZ COMPANY,
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March 16, 1905.

Determination of Nitrites in Waters.—Apropos of R. S. Weston's interesting notes upon this topic[1] it may be worth while to call attention to the fact that the "nitrite" error, due to the presence of burning Bunsen lamps, is often much greater than is suspected. In the water laboratory here the chemically pure distilled water is prepared by the use of a large copper retort heated by a very broad Bunsen burner. Only one other lighted burner is constantly in the room and that a small one. Distilled water, as delivered by the tin worm, was tested with the following results, duplicates being run in each instance. One Nessler tube was exposed to the room atmosphere, after addition of the "nitrite" reagents, and the other carefully protected therefrom. The results are stated as parts per million.

Conditions under which distilled water was collected.	Nitrites present in protected tube.	Nitrites present in unprotected tube.
Not allowed to come in contact with air of laboratory	none	0.0015
Slight contact with air. Tin condensing tube entering neck of receiving bottle	0.002	0.003
Water allowed to drop six inches through open air to receiving casserole	0.007	0.008

W. P. MASON.

RENSSELAER POLYTECHNIC INSTITUTE,
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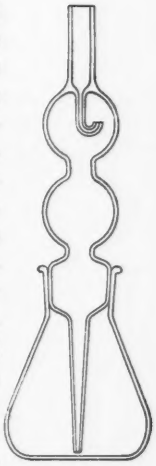
Pipette Weighing-bottle.—Among chemists who are called upon to analyze milk the need of a combination pipette and weighing-

[1] This Journal, **27**, 281.



bottle has often been felt. With this idea in mind Dr. H. M. Hill designed a pipette and bottle which admirably answers the purpose and has been found to be a great help in weighing milk for analysis. In laboratories where only analytical work is done or where each assistant or student has his own apparatus it would not be necessary to change the form of the apparatus as originally designed; but in large technical laboratories where a great variety of analytical, as well as commercial, work is being done, I found it necessary to make certain changes in this apparatus on account of the small ground cap, which is fitted over the mouth-piece of the two-bulbed pipette in the original form of the apparatus, being continually mislaid and very often lost. Sometimes the chemist using two or more pipettes will misplace the cap, thereby causing an error in the weighing, and the work must be begun anew. The improved apparatus obviates all these disadvantages and errors, and consists, as is seen in the drawing, of a weighing-bottle $1\frac{3}{4}$ inches in diameter in its widest part, $2\frac{1}{2}$ inches high and $\frac{3}{4}$ inch in diameter of mouth, into which is fitted a pipette $5\frac{1}{2}$ inches long, with three bulbs. The lower bulb acting as a stopper and the upper one having a small bent capillary tube inserted between mouth-piece and bulb, prevents evaporation. The pipette weighing-bottle weighs from 25 to 27 grams and has been found to be of excellent service in the analysis of oils and light liquids. For use in weighing heavy liquids, such as bark extracts and the like, the lip of this pipette and capillary tube must be of larger diameter.

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REVIEW OF PHYSICAL CHEMISTRY.

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Received February 20, 1905.

THE following article merely attempts to supplement the regular reviews of American Chemical Research, in this Journal, by citing the more important foreign work for the past year or more which falls within the somewhat loosely defined

field of physical chemistry. The mere investigation and description of individual substances and systems from the physico-chemical standpoint has become so general in the last few years that in such reviews as the present its treatment must for the most part be left to the inorganic or organic workers concerned with this or that particular class of bodies. In fact it may be fairly said that as fast as what we to-day term physical chemistry is reduced to definite laws, it ceases to directly concern the physical chemist proper and becomes the tool and method of the specialist in other fields.

The past decade and more has been marked by the development and wide-spread application of (*a*) the laws governing heterogeneous equilibrium (phase rule work as it is often called), (*b*) the electrolytic dissociatiou theory in the case of dilute aqueous solutions, and (*c*) the quantitative treatment of reaction velocities and homogeneous equilibrium. To-day electrolytic theories are taking on a new interest as investigation leaves the beaten path of dilute solutions turning to those of higher concentration, to non-aqueous solvents and even to solids and gases. As to reaction velocities it may fairly be said that except for the extension of the already established laws and methods to other fields, notably biology, we have for the past few years been practically at a standstill waiting for a clear conception of what may be termed chemical resistance or at least a method of directly expressing what it is that prevents chemical systems from coming immediately to true equilibrium. The Ohm's Law of chemistry still seems as far off as ever. Just as the broad thermodynamical considerations of Gibbs, Helmholtz, van't Hoff and others lead us to lay aside in many cases, as immaterial, distinctions between physical and chemical agencies and substitute for them the objective conceptions of "homogeneous" and "heterogeneous," so now in connection with the critical state and the colloids we are meeting with transitional phenomena which in turn seem often to evade classification and treatment under these very laws. It is interesting to note that these very limitations were clearly pointed out and discussed by Gibbs in his original memoirs in the seventies and in his treatment of surface phenomena, in the reviewer's opinion, will yet be found the key to the subject of colloids.

Passing to the individual contributions and beginning with those relating to the critical state we find quite an activity in the subject.

I. Traube and G. Teichner (*Ann. Phys.* (4), **13**, 595-619, 1904; *Z. anorg. Chem.*, **38**, 399-407, 1904) have busied themselves with the critical phenomena of pure liquids. They find the critical temperature of water (working in quartz tubes) to be 374°, as against 359° -364° of older observers. They also examined mercury up to 1000° C. without reaching its critical point. This lat-

ter confirms the observation of Strutt of a year or more ago. H. Happel (*Ann. Phys.* (4), **13**, 340–361, 1904), assuming parallelism of mercury and argon, has computed the critical temperature of mercury as 1370° absolute with a critical pressure of 456 atm. His paper also contains some interesting comments on the classes into which substances fall when viewed in the light of equations for corresponding states. The most interesting of the work of Traube and Teichner is, however, the experiment, carried out by the latter, of enclosing a number of glass spheres of different mean specific gravity in sealed tubes of carbon tetrachloride. At 1° above the critical temperature nearly 50 per cent. difference in specific gravity was found in different portions of the tube, the spheres distributing themselves from top to bottom; and at 6° above critical temperature 8 per cent. difference still remained.

Traube seeks for an explanation in a real difference between liquid and gaseous molecules ("Gasonen" and "Fluidonen"). In support of this he finds *b* of van der Waals' equation to differ for the gaseous and liquid states with "normal" liquids. His point of view here suggests strongly the recent work of T. W. Richards on compressibility of atoms (*Proc. Am. Acad. Arts and Science*, **37**, 3-17 and 399-411; **38**, 293-317; Abstract, this Journal, **23**, R. 159 and **24**, R. 441).

Another very suggestive treatment of the same subject is given by G. Baker (*Ztschr. phys. Chem.*, **49**, 609-617, 1904). The paper is the extension of a previous one on the theory of capillarity (*Ibid.*, **48**, 1-39, 1904), and points out from a purely mathematical standpoint that the physical region of discontinuity between gas and liquid should increase in thickness as temperature rises. In the neighborhood of the critical point this increase is very rapid, approaching infinity as a limit in the critical point itself. The apparent disappearance of the meniscus is therefore not a proof that the critical point in the sense of Andrews and van der Waals has been reached, and all the phenomena observed by Teichner lie really within the capillary layer which is expressly excluded in the development of van der Waals. Another point brought out by Teichner is the sudden change at the critical temperature in the temperature-"total heat," (*i. e.*, latent heat + specific heat) curve for a system of constant volume.

During the past year the critical point of two component systems has received much attention. Centnerszwer and Teletow (*Ztschr. Elektroch.*, **9**, 799-802, 1903), working on solutions in sulphur dioxide, and Smits (*Ibid.*, **9**, 663), working with solutions of anthraquinone in ether, have found cases of retrograde solution analogous to the well-known retrograde condensation; *i. e.*, as the temperature rises a homogeneous solution may deposit solid and at a higher temperature this solid passes back again into the fluid phase. Van der Waals has treated the matter in a

purely theoretical paper (*Versl. Kon. Ak. Amsterdam*, Oct. 31 and Nov. 28, 1903, **12**, 439-443 and 606-615; English translation, **6**, 230-244 and 357-366). In a second paper Centnerszwer (*Ztschr. phys. Chem.*, **46**, 427-502, 1903) shows that the critical temperature of the solvent is depressed by non-volatile solutes, according to the same law as the ordinary boiling-point, and gives the constants for several liquids. The dielectic constants and electrical conductivity of pure liquids and of solutions passing through their critical point have been investigated by Eversheim (*Ann. Phys.* (4), **13**, 492-511, 1904). He found a rapid decrease but no discontinuity. Kraus (*Phys. Rev.*, **18**, 40-56 and 89-103, 1904) found for alcohol solutions of alkaline haloids a sudden change in temperature co-efficient at the critical point when the tube was just full at this temperature. Van der Waals (*Versl. Kon. Ak. Amsterdam*, **12**, 82–110, 1903; English translation, **6**, 123–151 ; Abstract, see *Phys. chem. Centrbl.*, **1**, 231) has given us a review of the various attempts to improve on the original van der Waals equation. He now inclines to consider "*a*" as a constant and to work out "*b*" as a function of temperature and particularly of volume (Cf. T. W. Richards above). He thinks little of Traube's assumed difference between liquid and gaseous molecules.

In the matter of systems with two liquid layers and the point of total miscibility, Kuenen (*Phil. Mag.* (6), **6**, 637-53, 1903) has reviewed the field, especially as regards combined effects of pressure and temperature.

The liquid crystals of Lehmann, another border line phenomenon, are still a matter for dispute. Rotarski (*Phys. chem. Centrbl.*, **1**, 8) claims to have shifted the inversion point of *p*-azoxyanisol by further purification and considers it a mixture of the azo- and azoxy compound. Coehn (*Ztschr. Elektroch.*, **10**, 857), and Bredig and Schukowsky (*Ber. chem. Ges.*, **37**, 3419, 1904) tried electrical endosmose experiments upon them without success, also high centrifugal force with negative results. Tammann, in his book on crystallization and fusion, takes the stand that we have all grades of hardness in crystals from the diamond to the softest of the fatty acids and there is no reason why we should not go a step further and have crystals so soft as to be deformed into drops by their own surface tension. He therefore stands strongly for the name "liquid crystals" rather than "crystalline liquids."

F. G. Beilby, in a series of articles on the surface structure of solids (*J. Soc. Chem. Ind.*, **22**, 1166-1177; *Nature*, **70**, 31; *Proc. Roy. Soc.*, **72**, 18-232 ; *Electrochemist*, **3**, 806-819), brings forward strong evidence through electromotive force measurements, optical transparency and direct microscopic methods for the view that in the polishing of metals and even such substances as iceland spar, the surface undergoes a species of flow and becomes modified to an extent justifying us in considering it as an

allotropic form with reference to the main body of the material. The work of Spring (*J. Chim. Phys.*, **1**, 593, 1904) on the production of allotropic forms by great pressure also tends to bear out these conclusions.

Under the head of molecular weight determinations we meet some new and interesting solvents. Beckmann used bromine for boiling-point determinations of Al_2Br_6, the double formula being sustained (*Zischr. phys. Chem.*, **46**, 853-866). In the same article is a caution against methylene iodide as a solvent, as it crystallizes in two modifications whose melting-points only differ by 0.47°. Schenk and Buck (*Ber. chem. Ges.*, **37**, 915-917) have used phosphorus as a solvent for solid phosphine and obtain $P_{12}H_6$ as its formula. Bottomley (*J. Chem. Soc.*, **83**, 1421-1425) has used surface energy methods on fused salts and gives as association factors $NaNO_3 = 10.68$, $KNO_3 = 8.73$. Spercinski (*Ztschr. phys. Chem.*, **46**, 70-78), working with a new and delicate form of differential tensimeter, confirms by direct vapor pressure measurements Kuster's results on molecular weight of β-naphthol and napthaline in solid solution. Abegg and Labendzinski (*Ztschr. Elektroch.*, **10**, 77-78) give a convenient collection of data on complex building in metallic salt solutions, together with some new data. Bruni and Manuelli (*Ztschr. Elektroch.*, **10**, 601-604), also Lobry de Bruyn (*Akad. Amsterdam*, June 27, 1903, p. 91), have worked with hydrated and anhydrous chlorides of Mn, Co, Ni, Cu and other salts in urethane, as solvent with no dissociating power, and in acetamide, as solvent with high dissociating power. In urethane salts they gave normal values, many holding all or part of their water of crystallization. In acetamide they all showed strong dissociation.

Much of the work on electrolytes in non-aqueous solvents has already been referred to in this Journal (**27**, 65). In addition may be mentioned the very complete work of Walden (*Ztschr. phys. Chem.*, **46**, 103-188, 1903), consisting of quantitative measurement of conductivity and dielectric constant of fourteen classes of organic solvents, all specimens being purified with great care. All the solvents used, when sufficiently pure, gave surprisingly similar values for their own conductivity. κ_{25} = from 1 to 5×10^{-7}, with some four or five exceptions, where the values were about one hundred times greater. The highest conductivities are generally found in OH and CO compounds. A thorough review of earlier work is given and another paper promised. Mittasch (*Ztschr. phys. Chem.*, **46**, 37-42, 1903) finds $Ni(CO)_4$ to be a very poor electrolytic solvent. Its dielectric constant is 2.2 and its molecular weight is normal. Joh. Schroeder (*Habilit. Schrift. Giessen*, 1904, p. 58; *Phys. chem. Centrbl.*, **1**, 591) has studied the reactions and molecular weights of Ag, Hg, Cu and Fe halides in pyridine. A general summary and extensive bibliography of

the subject up to September, 1903, is given by P. Dutoit (*J. Chim. Phys.*, **1**, 617-656, 1904).

The question of the absolute potential of a single electrode has been taken up again of late by Billitzer (*Wien Akad Ber.*, **112**, 1553-1595; also *Ztschr. phys. Chem.*, **48**, 513-548). He used at first the mercury dropping electrode, but in a somewhat different manner from previous observers. Its potential was maintained from without at various values and by direct chemical analysis the point was determined at which mercury was neither given to or taken from the solution. The neutral point for the particular arrangement used was thus located between —0.37 and —0.43 (H in $\frac{N}{1}H_2SO_4=0$), agreeing well with —0.4, as given by the previous work on electrical endosmosis (Wurtzburg meeting of Bunsen Gesellschaft). A second method depended upon setting up currents by suddenly extending or contracting a mercury surface in the electrolyte. The current changes sign twice, *viz.*, at +0.35 and —0.4 volt. Between two mercury electrodes in the same solution a current flows if the electrolyte, over one electrode, is kept in motion. This current reverses its direction when the electrodes are brought to a potential of —0.4 volt, but not at +0.35 volt, from which the author concludes that the latter point is due to changes in surface tension due to stretching and contracting the surface. He urges the point —0.4 volt as the true absolute neutral. Wulf (*Ztschr. phys. Chem.*, **48**, 87-96) has confirmed the Helmholtz formula for gas electrodes between 1 and 1,000 atmospheres. Muthmann and Fraunberger (*Sitzber. bayr. Akad.*, **34**, 201-241, 1904; *Phys. chem. Centrbl.*, **1**, 695) investigated the cause of the passive state of iron and other metals and attribute it to a film of oxide. Even very short contact with the air produces some effect. They claim that generally accepted single potentials for iron and some other metals are vitiated by this and redetermine the same under special precautions. Hollis (*Proc. Cambridge Phil. Soc.*, **12**, 253 and 462-465, 1904) shows that passive state can only be produced below a certain temperature for each metal, Fe a little below 100° C., Ni about 72° C., and Co about 10° C. A general review of the whole subject and discussion of the theories advanced is given by Sackur (*Chem. Ztg.*, **28**, 954-956, 1904).

The possibility of making a sharp analytical separation even on a mercury cathode is proved by Coehn and Kettembeil (*Ztschr. anorg. Chem.*, **38**, 198-231) for the alkaline earths. Strontium required 0.2 volt more than barium, and calcium 0.25 more than strontium to deposit it. Wedekind (*Chem. Ztg.*, **28**, 268-270) applies this same principle to separate radium from barium, but does not seem to consider it a practical method (see also Marckwald, *Ber.*

chem. Ges., **37**, 88-91). Siemens (*Ztschr. anorg. Chem.*, **41**, 249-275) has investigated to what extent Na, K, NH_4, Li, Be and Al may be made to alloy with Ni, Co, Fe, Zn, Cd, Sn, Cu and Ag. Positive results were only obtained in the case of Mg with Ni, Fe, Co and Zn, the alkalies with Ni and Sn and possibly NH_4 with Ag. As much as 3 per cent. Mg may come down with Ni, a fact which is made use of in securing specially coherent deposits in Ni plating. Numerous attempts have been made to apply alternating currents to electrolytic processes. Blochet and Petit (*Compt. rend.* **128**, 419-421 and 1095-1097) reached 50 per cent. current efficiency for the solution of Pb in H_2SO_4 and also succeeded well with Pb, Co and Fe in KCN. In KCN solution with 20-80 amp. per square decimeter 0.4-0.6 gram per hour was dissolved. Pierce and Couchet (*Compt. rend.*, **138**, 361-363) have applied alternating currents to reduction of nitrates, chromates and nitrobenzene with technical ends in mind. The best systematic treatment that has appeared is by Le Blanc and Schick (*Ztschr. phys. Chem.*, **46**, 213-243, 1903). They studied chiefly the effect of varying frequency, current density and concentration. Incidentally they arrived at an estimate of the velocity of formation of complex ions. With $\frac{N}{10}$ Cu″ and $\frac{N}{1}$ CN combination was practically complete in 0.001 minute while with $\frac{N}{800}$ Cu″ at end of $\frac{1}{80000}$ minute practically no combination had occurred. Schlomilch (*Elektrotechn. Ztg.*, **24**, 959, 1903) describes an electrolytic coherer. Its essential feature is an anode consisting of a fine platinum or gold point in sulphuric acid. A polarizing electromotive force is applied in just sufficient amount to effect visible electrolysis. When the point is subjected to electrical waves the residual current greatly increases only to fall back again when the electric waves are cut off. Rothmund and Lessing (*Ann. Phys.* (4), **15**, 193-231) have since carried out a more systematic study of the phenomenon and determined the best conditions. They find the effect both at anode and cathode and explain it on the grounds that the electric oscillation periodically increases and decreases the potential on the electrodes. When the potential due to the wave is added to that of the polarizing battery a current flows; when opposed no current flows. In other words the cell acts toward the electric waves much as the aluminum plate of the ordinary electrolytic rectifier (see Norden: *Ztschr. Elektroch.*, **6**, 159-167 and 188-202). Electrolytic conduction in solids has received considerable attention since the advent of the Nernst lamp but most of the work has been of a commercial type and consequently little has found its way into print. Reynolds (*Dissert. Göttingen*, 1902; also a brief abstract in *Nachrichten Göttingen Akad. d. Wiss.*

Nernst and Reynolds, 1900, p. 330). In the matter of electric discharge through gases Stark and Cassuto (*Phys. Zeit.*, **5**, 264-269) have tried the effect of cooling the electrodes in various ways and find that the anode may be cooled to any degree without affecting the arc but that slight cooling of the cathode breaks the current. This agrees well with the theory of discharges of negative ions from the hot cathode. Monash (*Dissert. Darmstadt. Hochsch.* See *Phys. chem. Centrbl.*, **1**, 168) has studied effect of length of arc on its potential, using an alternating current of 0.02-0.06 amp. between various metals. The superposition of disruptive discharge upon the true arc is brought out and the great effect of small impurities of carbon in the metals noted. Kerkby (*Phil. Mag.* (6), **7**, 223-232) has studied the effect of the current from a charged zinc plate illuminated with ultraviolet light on a mixture of hydrogen and oxygen at low pressure but found no appreciable combination up to the sparking potential. The author then speculates on the mechanism of combination for these two substances.

J. J. Thomson (*Phil. Mag.* (6), **7**, 237-265, 1904) has brought forward a rather daring attempt to explain the structure of the elements in harmony with the periodic system and the recently discovered facts of radioactivity. He pictures the atoms as built up of negative electrified corpuscles within a sphere of uniform positive electrification. Then from the principles of mechanics works out the possible stable arrangements of such a set of particles and attempts to connect these with the known properties of the various elements.

Out of the great mass of spectroscopic work may be noted as of special chemical interest the following: von Bolton (*Ztschr. Elektroch.*, **9**, 913-922, 1903) describes the spectra produced at the surface of a metallic conductor and electrolyte on the passage of a 110-volt current of high density. A more exact and detailed account of similar phenomena with the Whenelt interrupter by Morse (*Astrophys. Jr.*, **19**, 162-186) has appeared in this country.

Nasini and Anderlini (*Rend. R. Acc. di Lincei* (5), **13**, 59-66; *cf. Phys. chem. Centrbl.*, **1**, 653) claim to have obtained emission spectra of nitrogen and iodine by simply heating the gases in an electric furnace. Magini (*Phys. Zeit.*, **5**, 145-147), also Baly and Desch (*J. Chem. Soc.* (London), **85**, 1029-1041), working in the violet, and Ikli (*Phys. Ztschr.*, **5**, 271-277), in the infra red, have sought for a relationship between absorption bands and chemical constitution; the former with positive but the latter with negative results.

Turning to photochemistry and photography we find Liesegang (*D. photo. Ztg.*, **28**, 102-104; abstr. *Phys. chem. Centrbl.*, **1**, 208) attempting to explain the great difference in the thinning of the image in the hypo-bath, observed when different developers

are used, on the ground that the powerful developers reduce directly to metallic silver, while with the weaker ones only the sub-halide stage is reached. Lumiere and Seyewetz (*D. photo. Ztschr.*, **28**, 185-188; *Phys. chem. Centrbl.*, **1**, 371) point out that only those reducing agents are able to act as developers with sodium sulphite alone (without alkali) which have an amino group in the benzene nucleus and they lose the power if a substitution is made in the group which greatly reduces its basic nature. Kirchner (*Ann. Phys.* (4), **13**, 239-270) has studied the structure of the film of the Lippmann color plates, particularly the refractive indices of gelatin and silver, and concludes that about one-third of the available silver is reduced and that it makes up about 1/300 of the total thickness of the film. He believes the silver to be truly massive and not "molecular," as has been suggested by some. Luther and Weigert (*Berlin Akad. Ber.*, 1904, pp. 828-839) have studied from the standpoint of reaction velocity the polymerization of anthracene dissolved in boiling phenetol. In the light the polymerization proceeds and in the dark the action is reversed. So few reversible photochemical reactions are known and these have been so little studied that this homogeneous system becomes of special interest. The homogeneity of the system has, however, been questioned by Nernst (see Breslau meeting of Deutsch. Naturf. u. Aertzte., Sept., 1904) on the ground that the light must vary in intensity as we proceed into the mass of the liquid. The authors find the reaction to be monomolecular and the constants in both directions were determined. For equilibrium they found the relation: conc. of dianthracene = const. $\frac{\text{(Intensity of light)} \times \text{(surface exposed)}}{\text{volume of solution.}}$

It is notable that the final concentration of the dianthracene appears to be independent of the concentration of the anthracene. Further work is promised. Byk has given us a very interesting theoretical paper (*Ztschr. phys. Chem.*, **49**, 641-687) on the photochemistry of optically active bodies and the possibility of producing active bodies by purely physical means, *viz.*, circularly polarized light. He shows that due to the inclination of the earth's axis there is a slight predominance of circularly polarized light of the one sign over that of the reverse sign. It has been shown experimentally that optical isomerides absorb right and left circularly polarized light to different extents and photochemistry has shown that absorption and photochemical action run parallel wherever the latter exists. From this chain of laws the authors explain why we have in plant and animal substances one of the optical antipodes instead of the racemic mixture characteristic of our laboratory syntheses. The experimental part of the paper aimed at the direct production of an active body from a racemic mixture by photochemical means gave negative results. This may mean that the examples were poorly chosen or that the effects

in a single instance are too small to be appreciable, and it is by the cumulative process, which the author points out is to be expected in nature, that the effects become appreciable. Schaum and Braun (*Ztschr. wiss. Photog.*, **1**, 377-384) have worked with plates free from gelatin and find such phenomena as solarization to exist there as well, so that their explanation is not referable to the gelatin. Röntgen rays were also active on a film of silver bromide on platinum, so the theory of fluorescence of the glass or gelatin in their case must now be discarded. In the study of the selenium cell the theory which attributes its action to traces of metallic selenides seems to be losing ground. Berndt (*Phys. Ztschr.*, **5**, 121-124) and Pfund (*Phil. Mag.*, (6), **7**, 26-39), both working with graphite electrodes, reject it. The former attributes the change of resistance to displacement of equilibrium between two crystalline modifications of the selenium itself. The latter measured the sensitiveness with various admixtures of metallic selenides and found the point of maximum sensitiveness in the spectrum to be independent of their presence or nature. Marc (*Ztschr. anorg. Chem.*, **37**, 459-474) comes to the same conclusion as Berndt, from studies of the temperature coefficient of the cells in different parts of the spectrum.

The more important data concerning radium and radioactivity have been given in the review on inorganic chemistry (this Journal, **27**, 63), and a comprehensive review would carry us beyond our limits. For such review see book list at end of this article, also W. Crooks "Modern Conceptions of Matter" (*Chem. News*, **87**, 277-281) in his address at Berlin Congress of Applied Chemistry; Rutherford, Bakerian lecture before the Royal Society, May 19, 1904 (*Proc. Roy. Soc.*, **73**, 493) and also a review by Curie himself (*J. Chim. Phys.*, **1**, 409-449; and *Phys. Ztschr.*, **5**, 281-288; 313-318; 345-349). The theory which has fast been gaining ground that radium was constantly being formed by the disintegration of uranium and in its turn passing on to simpler bodies, among them helium, seems to have met with a set back as far as the first step is concerned, from the work of Soddy (*Nature*, **70**, 30). He purified a kilo of uranium nitrate until it contained less than 10^{-13} grams of radium. At the end of a year not more than 10^{-11} grams had accumulated (this being the limit of sensitiveness of his instruments at that time). If the radioactivity of uranium is due to its decomposition into radium, according to the above theory, we should look for about 5×10^{-7} grams to be produced in the above experiment. Giesel (*Ber. chem. Ges.*, **36**, 342, and **37**, 1696-1699) believes he has another radioactive element bearing the same relation to lanthanum that radium does to barium, and calls it "emanium." It acts much more strongly in the spinthariscope than radium does. Its source is also pitchblend. Ramsay and Cook (*Nature*, **70**, 341-342) describe the coloring of glass by radium and the extraction of an emanation

from the glass by solution in water, and suggest it may be a case of reversal of the radioactive development, by conversion of the energy of the radiation back again into chemical energy, the glass, in fact, acting as a sort of storage cell.

Among other papers on the chemical action of radium rays may be mentioned: Pellini and Vaccari (*Atti. R. Ac. Lincei* (5), **13**, 269-275), working with hydroiodic acid and with propyl and isopropyl iodides, got positive results and attribute the action to the γ-rays. With H+Cl and the photometer solutions of Neiper de St. Victor and Roussin (see Eder *Jahrb. d. Photo.*, 1891, pp. 370-382) they got negative results. Hardy and Willcock found a strong oxidizing action of the rays on iodoform (*Proc. Roy. Soc.*, **72**, 200-204; *Ztschr. phys. Chem.*, **47**, 343-352). They attribute the greater part of the action to β- and some to easily penetrating γ-rays. Sunlight worked somewhat more strongly and the authors attribute the violent physiological action of radium rays to their penetrating power. Hardy (*Proc. Physiol. Soc.*, p. 29; *J. of Physiology*, **29**, 1903) has also shown the powerful coagulating effect of the radium emanation on an alkaline solution of the globulin from ox serum. An acid solution of the same became clearer and lost its opalescence. Tenton (*Proc. Camb. Phil. Soc.*, **12**, 424-426; *Phys. chem. Centrbl.*, **1**, 425) finds H_2O_2 decomposes about twice as fast when exposed to $RaBr_2$ as when left alone in the dark. The so-called "N-rays" first reported by Blandlot as emitted from hot bodies and later from a variety of sources, such as contracting muscles, have attracted a considerable amount of attention, but at present seem to be considered by the majority of serious workers as purely subjective phenomena (see Schenk, McKendrick and Colquhoun: *Nature*, **69**, 486 and 534; also Lummer: *Phys. Ztschr.*, **5**, 126-128).

Armstrong and Loury (*Proc. Roy. Soc.*, **72**, 258-264) note that saccharin crushed under an opaque screen of barium platinocyanide or zinc blende produces brilliant flashes of light; also menthylphenylformylacetate produces flashes of light on crushing or crystallization from light petroleum. They assume labial and stable forms and believe that a change of the one form to the other is responsible for the phenomena. Gutton (*Compt. rend.*, **138**, 268-270, 352-353, 568-569) finds the luminosity of calcium sulphide increased by being placed in a variable magnetic field. A uniform field has no effect. He claims the phenomenon is very delicate and uses it to show magnetic effect of convection currents. Hemptine (*Compt. rend.*, **138**, 754-755), however, tried it with negative results, but suggests that his sulphide may not have been sufficiently sensitive. Schmidt (*Ann. Phys.*, (4), **13**, 622-633; see also **9**, 707) finds that if oxides of aluminum and zinc are pure they show no fluorescence in the canal rays of a discharge tube, but the least trace of foreign oxide produces fluorescence, the color depending on the kind of oxide. In light

of these facts the work of Wein and Tafel is criticized. See also a reply by Tafel (*Ann. Phys.* (4), **14**, 206).

The literature of colloids and colloidal solutions has received many additions of late, but as a comprehensive review of this field appeared in the October number of this Journal (Whitney and Blake: **26**, 1339-1344) little more need be noted here; see, however, bibliographies at end of this article. Duclaux, in a series of articles in the *Comptes rendus*, has endeavored to show that coagulation at least in the case of metallic hydroxides is due, in great part, to actual change in chemical constitution or composition. His work is collected in a thesis of 112 pages, presented to the Faculty of Science of Paris. (Abstract in *Phys. chem. Centrbl.*, **1**, 727). Ramsden (*Dubois-Raymonds Archiv.*, 1904, p. 517; *Proc. Roy. Soc.* (London), **72**, 156-164; *Ztschr. phys. Chem.*, **47**, 336-346) has studied the surface structure of colloidal solutions and pointed out the coagulating effect of shaking. He finds a surface film of higher concentration in all the colloidal solutions studied. Schutt (*Ann. Phys.* (4), **13**, 712-746), working principally on glycerol and soap solutions, rejects the explanation of a surface layer of greater viscosity and treats the liquid as a heterogeneous system. Bütschli (*Ber. d. k. bayr. Akad. Wiss.*, **33**, 215-230, 1903) finds that solutions of dextrin and gums in 65 to 70 per cent. alcohol on drying show cellular structure and urges this as evidence that the liquids really consist of two phases. The most striking departure in the study of colloids is perhaps the use to which some optical methods have of late been put. Lobry de Bruyn and Wolff under the title "Can the molecules in solution be demonstrated by the optical method of Tyndall"? (*Versl. k. Ac. Wet. Amsterdam*, **12**, 778-788; *Rec. Trav. Chim.*, **23**, 155) point out that the diameter of particles of colloidal suspensions or solutions, as usually calculated, are only some tenfold greater than the commonly accepted figures for chemical molecules (*Cf. Lobry de Bruyn, Rec. Trav. Chim.*, **19**, 251). They then apply a beam of light filtered through picric acid (to avoid danger of fluorescence) to solutions of inorganic salts, alcohol, acetamide, etc., but observe no reflections. In the case of various sugars in aqueous solution and benzoic esters of mannite and other poly-acid alcohols in organic solvents they obtain reflections and believe the question can be answered in the affirmative. A somewhat similar paper by Rachlmann (*Berl. Klin. Wochensch.*, No. 8, 186-190, 1904; abstract in *Phys. chem. Centrbl.*, **1**, 426) states that with the Siedentopf and Zsigmondy microscope (*Ann. Phys.*, (4), **10**, 1-39), he was able to watch the breaking-up of glycogen aggregates by diastase solution. He also mentions seeing some submicroscopic bacteria feeding on molecular complexes of albumin solutions. How much allowance must be made in these cases for subjective influences the reviewer hesitates to say. Bredig and Weinmayer

(*Boltzmann Festschrift*, 839-847) have measured the total surface of colloidal particles of gold in solution by amalgamating them through the addition of alkaline mercuric chloride solution and then measuring the rate of catalysis of hydroperoxide. The latter has been shown to be directly proportional to the surface of mercury exposed. Further, from the known amount of mercury added the thickness of the film may be computed. The minimum amount of mercuric chloride which produced the full effect corresponds to a film 3×10^{-8}, which agrees well with our accepted order of molecular dimensions.

The applications of physical chemistry to biology in the past two years make quite a chapter in themselves. In fact, the biologists are often more sanguine and enthusiastic in the application of physico-chemical principles than the physical chemists themselves. All that can be attempted here is to note a few representative articles as indications of how physico-chemical ideas are making themselves felt in biology. The particular branch which of late has perhaps attracted most attention is that of toxins and antitoxins. Arrhenius and Madsen (*Ztschr. phys. Chem.*, **44**, 7-62, 1903; and *Centrbl. f. Bakt.*, I Abt., **34**, 630-641, 1903) pointed out that certain, at least, of the antitoxins—particularly that of tetanus—accomplished their results by directly uniting with their corresponding toxins to form easily dissociable compounds which are subject, as far as their dissociation is concerned, to the ordinary mass law. This furnishes an explanation of the fact that the first small addition of antitoxin depresses the poisonous effect of the toxin far more than equal succeeding additions. This fact had previously led Ehrlich to assume (particularly for diphtheria) a complex nature for toxins such that one after another of the various bodies, of which he supposed them to be composed, were neutralized by the antitoxin, the first to be neutralized being the most virulent. When Madsen and Arrhenius extended their investigations to the diphtheria toxin and showed that the mass law was capable of explaining all the results obtained by Ehrlich, the latter combated their views vigorously and interested a number of other physiologists, as well as physical chemists, in the controversy. A number of the more important articles on the matter by Ehrlich, von Dungern, Sacks, Keys, Morgenroth, Nernst, Arrhenius, Masden, Walburnand and Koeppe are collected and reviewed by Aron (*Phys. chem. Centrbl.*, 1, 487-492), and a very fair idea of the details of the situation can there be had. Arrhenius and Masden seem to have pretty well made good their original stand. Perhaps the most striking proof of their theory, as far as regards the dissociation of the compound of toxin with antitoxin, lies in an experiment in which, out of an inert mixture of toxin and antitoxin, by simple diffusion (in gelatin), the free and virulent toxin was obtained owing to its rate of diffusion being greater than that of the antitoxin

and of the compound of the two. The applications of gas-cell measurements to blood by Höber (*Pflug. Archiv.*, **81**, 522, and **99**, 572-593), Fränkel (*Ibid.*, **96**, 601), and Farkas (*Ibid*, **98**, 551-576) have led, after some controversy, to agreement on its complete neutrality. Höber's first measurements were vitiated by the currents of hydrogen, used to saturate the electrodes, removing carbon dioxide and thus producing artificially an alkaline reaction. In his last set an amount of carbon dioxide, corresponding to its partial pressure over the normal blood, was added to the hydrogen from the start. Farkas worked with closed electrodes, and Fränkel with palladium electrodes, previously saturated with hydrogen by electrolysis. Friedenthal (*Ztschr. allgem. Physiol.*, **4**, 43-61) has applied his indicator methods (see below) to various body fluids, finding them nearly all neutral. The equilibrium between oxygen and haemoglobin still continues to occupy several workers; see Loewy (*Archiv. Anat. u. Physiol.*, 1904, pp. 166 and 231), and Bohr (*Centrbl. Physiol.*, **13**, 713-715, and **17**, 682-688). In the matter of electro-physiology, electromotive force produced by diffusion through a semipermeable wall (see Ostwald, *Ztschr. phys. Chem.*, **6**, 71, 1890) is beginning to attract more attention. Brünnings (*Pflug. Archiv.*, **100**, 367-427) points out that though the ordinary fluid concentration cells are capable of producing only a very slight electromotive force when a diaphragm is introduced which is only permeable to one of the ions of a compound, very small differences of concentration are able to produce quite appreciable effects and that in the organism many such combinations may be arranged in series as it were. Höber (*Pflug. Archiv.*, **101**, 607-663, and **102**, 196-205) makes use of somewhat similar conceptions, together with the phenomenon of electrical endosmose to explain the passages of body fluids through a membrane, apparently against the osmotic pressure.

Three very welcome papers on the absolute value of the "end-point" with various indicators, have appeared by Friedenthal, Salessky and Fels (*Ztschr. Elektroch.*, **10**, 133-119 and 204-214). The first two workers employed gas cell methods to determine the concentration of H and OH ions, while Fels checked these results by an application of the mass law to mixtures of salts with weak acids and bases. The measurements on the whole agree fairly well with one another, though the authors take issue on some points as, for example, the effect of concentration of the indicator itself. Friedenthal's work covers not only the region immediately about the neutral point, but supplies a list of indicators with end-points all the way from twice-normal acid to twice-normal alkali. The discussion of, and the practical suggestions upon, the methods of preparing standard solutions of very slight acidity and alkalinity are particularly interesting and suggestive. Vaillent (*Compt. rend.*, **137**, 849-851, 1903) has

measured the electrical conductivity and the spectral absorption of methyl orange solutions, and finds their relation not in harmony with either Ostwald's theory of colored ions or that of Küster (*Ztschr. anorg. Chem.*, **13**, 127-150, 1897). He explains the changes on the ground of a molecular rearrangement in presence of acid (see Steiglitz, this Journal, **25**, 1112-1127).

Out of the great mass of reaction velocity determinations now appearing may be mentioned here a dynamic study of the Friedel and Crafts' reaction by Steele (*J. Chem. Soc.*, **83**, 1470-1480). Cases are pointed out where the reaction appears as monomolecular and others of the bimolecular type and inferences drawn concerning the intermediate compounds. Slator (*Ztschr. phys. Chem.*, **45**, 513-536) has made a systematic study of the rate of chlorination of benzene in the light and in presence of various catalyzers. In every case in the dark the viscosity was directly proportional to the concentration of the chlorine. In the light, however, it was proportional to the square of the chlorine cone (*Cf.* here Bodenstein, *Ztschr. phys. Chem.*, **22**, 23, 1897). Stannic chloride and ferric chloride accelerated in proportion to their concentrations. With iodine monochloride the velocity was proportional to the square of its concentration. Quartoroli (*Gaz. chim. Ital.*, **34**, 505-516; *Phys. chem. Centrbl.*, **1**, 564) finds the temperature coefficient for saponification of methyl and ethyl acetate to vary abnormally near the temperature of maximum density of water and the irregularity to follow this point, as the latter is depressed by addition of alcohol. A series of five articles, by Lobry de Bruyn, Steger and Tijmstra (*Ztschr. phys. Chem.*, **49**, 329-367), deals with the alcoholates as regards their reaction velocity with other bodies and their electrical conductivities. Reactions of the type $RI + NaOR_1$ appear to be ion reactions. Those of the type $C_6H_4(NO_2)_2 + NaOR$ to be more complicated in mechanism. Incidentally, the rather surprising fact is brought out that in distributing itself between water and alcohol, even in weak alcohol, the greater part of the sodium is probably there as alcoholate.

The study of reaction velocity in heterogeneous systems has received considerable impetus from a paper by Nernst (*Ztschr. phys. Chem.*, **47**, 52-55), pointing out how the phenomena as a whole must be resolved into (1) diffusion to and from the surface of discontinuity, and (2) the real reaction velocity in the homogeneous phases. Following this paper is one by Brunner (*Ibid.*, **56**, 103), working in Nernst's laboratory, on the rate of solution of various solids and the electrolytic reduction of iodine. In this the above theory is applied to practical cases with satisfactory results. Haber (*Ztschr. Elektroch.*, **10**, 156-157) points out the application of the above to his former work on rate of attack of glass surfaces by water and concludes that much of the reaction observed by him took place within the glass as solid solution or viscous liquid. Hantzsch (*Ztschr. phys. Chem.*, **48**, 289-329)

treats of the reaction of ammonia gas on the solid organic acids from the same standpoint. Hertzog (*Ztschr. physiol. Chem.*, **41**, 416-424), considering enzymes as constituting a second phase in the solutions to which they are added, treats the whole problem of enzyme reactions in the light of the above and sees in it an explanation for the predominance of the monomolecular type. Schurr (*J. Chim. Phys.*, **2**, 245-306) has treated the rate of solution of salts in their own and other solutions from another standpoint, but as he employed no stirring whatever it is hard to compare his results directly with those of the other workers.

The first well-defined reaction in a homogeneous solid (*i. e.*, crystalline system) has lately been given us by Ciamician and Silber (*Ber. chem. Ges.*, **34**, 2040-2046, 1901) in the passage of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid, which takes place without disturbing the crystal form in the process. The work has been confirmed by Lobry de Bruyn and Jungius (*Rec. Trav. Chim.*, **22**, 298, 1903). Starting from this suggestion, Bruni and Callegari (*R. Acc. d. Linc.*, **13** (5), 567-573; see *Phys. chem. Centrbl.*, **1**, 448) have studied a large number of nitro and nitroso derivatives of aromatic bodies by the crysocopic method and found the formation of mixed crystals between them a very general phenomenon. In this connection may be mentioned an article by Sachs and Hilpert (*Ber. chem. Ges.*, **37**, 3425-3431, 1904), pointing out that the above photochemical reaction is characteristic for *o*-nitro compounds.

Vondráček (*Ztschr. anorg. Chem.*, **39**, 24-40) finds that if platinum occludes oxygen it oxidizes hydrogen in both ammonium salts and ammonia. If the platinum is free from oxygen it reduces nitrous acid. The author believes this typical for other cases of platinum catalysis.

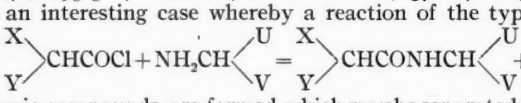
Luther and Schillow (*Ztschr. phys. Chem.*, **46**, 777-817) have given a comprehensive treatment of induced reactions. Such systems may be illustrated by the oxidation of arsenious oxide ("acceptor") by hypobromous acid ("actor") which does not take place by itself, but does take place if sulphurous acid ("inductor") is being oxidized at the same time. This case is explained by intermediate formation of bromous acid, which oxidizes arsenious oxide directly. In the paper it is pointed out how common this type of reaction is and how, by suitable velocity measurements, the mechanism and the intermediate products may be determined.

In the field of equilibrium in heterogeneous systems the work on alloys has, perhaps, been attracting most attention, but the greater part of it consists of accumulation of data for individual systems and cannot be here reviewed to advantage. The amount of data in this field is fast getting to the point where something analogous to the Beilstein in organic chemistry is a necessity. A rather new departure in the experimental side

of the work is the study of the distillation of alloys by Moissan and O'Farally (*Compt. rend.*, **138**, 1659-1664). Copper and lead form two immiscible layers. Lead and tin give a system comparable with alcohol and water, and copper and tin give one comparable with formic acid and water, having a maximum boiling-point. The first volume of the collected work on the Stassfurt salts, which has occupied van't Hoff and his students for some years, has lately appeared. It contains the data for the simpler systems already published in the *Sitzungsbericht* of the Prussian Academy. The work on calcium sulphite in its various forms was summarized in a single article some time ago (*Ztschr. phys. Chem.*, **45**, 257-306). In this connection see also Rohland (*Ztschr. anorg. Chem.*, **36**, 332-339) concerning the setting of plaster of Paris and the catalysis of the same. Wittorf (*Ztschr. anorg. Chem.*, **39**, 187-196) has studied the equilibrium of silicon dioxide in fusion of alkaline carbonates at 780° and 825° C., and finds the dissociation pressures for the carbon dioxide to decrease in the order Li, Na, K, Rb, Cs. Smith (*Ztschr. anorg. Chem.*, **37**, 332-336) has made a corresponding study in potassium and sodium carbonates with SiO_2, TiO_2, ZrO_2 and ThO_2 as solid phase, and finds at 900° and atmospheric pressure for carbon dioxide, the degree of combination falls off in the order above given. Tammann (*Ztschr. anorg. Chem.*, **37**, 448-454) shows that the inversion point from α to β iron (at 770°) is not affected by pressure, while that from α to γ (at 890°) is lowered 0.0029° for every $\frac{\text{Kilo}}{cm^2}$ and at 12,000 $\frac{\text{Kilo}}{cm^2}$ the α- β- and γ-forms may be in equilibrium together. At 1/100 of the earth's radius below the surface the pressure is 6,000 atmospheres, corresponding to a magnetic inversion at 600° and the interior of the earth cannot, therefore, be magnetic as far as iron is concerned. In the mutual solubilities of liquid phases Hudson (*Ztschr. phys. Chem.*, **47**, 113-115) has given us a new and interesting case in nicotine and water. At room temperature they are miscible in all proportions, at 60° they separate into two layers, at 90° what was at first the lighter layer becomes the heavier and sinks to the bottom, and at 210° they are again miscible in all proportions. In the determination of the solubility of slightly soluble substances Böttger (*Ztschr. phys. Chem.*, **46**, 521-619) has given us much new data from conductivity measurements and a critical discussion of the errors of the method. The substances, some thirty in all, are silver, lead and calcium salts. Starting from the work of Richards (this Journal, **23**, R. 159, and **24**, R. 441) on change of heat capacity during reaction, van't Hoff (*Boltzmann Festschrift*, pp. 233-241) has treated the particular case of melting and transition points, showing that by taking account of this factor we may explain the apparent exceptions (see Bodlander, *Ztschr. Elektroch.*, **8**, 835, 1902) to the rule that endothermic reactions become more

complete as the temperature rises and vice versa. A very satisfactory review of the whole subject is to be found in *Ztschr. Elektroch.*, **10**, 633-642, 1904.

In structural chemistry Elbs (*Ztschr. Elektroch.*, **10**, 579-583) has shown that we may have structural obstacles to electrolytic reductions just as we have in purely chemical reactions. Wedekind (*Ztschr. phys. Chem.*, **45**, 235-248) has given a general view of the optical activity of pentavalent nitrogen. A similar review of the work up to date and some new data on compounds of the type of $NR_2R'R''R'''$ is given by Aschan (*Ztschr. phys. Chem.*, **46**, 293-322). Mohr (*Ber. chem. Ges.*, **37**, 2702-2704) points out an interesting case whereby a reaction of the type



mic compounds are formed which may be separated by the ordinary methods without the help of optically active acids and bases and thus the activity of the fundamental compounds indicated without actually separating them as such.

It is gratifying to notice how the geologists and metallurgists are beginning to apply phase rule methods to the problems of fusion and solidification of rocks and slags. For a summary and discussion of some of this work see Vogt (*Videnskab.-Selsk. Skrifter*, No. 8, 1903) who has also published a separate book (see list below) and Jüptner (*Tscherm. min. u. pet. Mitt.*, **23**, 180-214, 1904). An attempt to work out a general rock classification on this basis has been made by Osann (*Ibid.*, **19**, 351; **20**, 399-558; **21**, 365-448; **22**, 323-356), but as yet it is more suggestive than practical.

The effect of centrifugal force on equilibrium in solution has been investigated by van Calcar and Lobry de Bruyn (*Versl. k. Acad. v. Wet. Amsterdam*, **12**, 1903, (4), 936-940; *Rec. Trav. Chim.*, **23**, 218; *Phys. chem. Centrbl.*, **1**, 518). With a centrifugal force equal to 400 times gravity they succeeded in causing considerable crystallization from solutions of Na_2SO_4, KCNS, K_4FeCN_6, KI and sugar. The magnitude of the effect reported is surprisingly great. Further work is promised.

The problems connected with ozone seem to have attracted special interest of late. The most striking departure is perhaps the theory—which has gained pretty general acceptance—that the formation of ozone by the brush or the silent discharge, as in most of our practical ozonizers, is due not to any direct electrical action on the oxygen itself, but is simply a photochemical effect, due to the very high ultraviolet light accompanying such discharges. The best proof of this lies in the fact that a vacuum tube or a mercury arc lamp, made of pure quartz when lighted up by the discharge, produces powerful ozonization in the surrounding air. The transparency of quartz to these rays is, of

course, well known. Goldstein (*Ber. chem. Ges.*, **36**, 3042-3046) found that a Geisler tube of oxygen under a few centimeters pressure immersed in liquid air, when excited, condensed ozone on its inner walls in blue drops, the pressure falling to a small fraction of a millimeter. If oxygen were steadily admitted to maintain the original pressure, a continuous formation of liquid ozone could be maintained. Clement (*Ann. Phys.* (4), **14**, 344-353) attempted to prepare ozone by passing oxygen through a hollow Nernst lamp filament (temperature 2200°) and quickly chilling it on emerging, but he obtained negative results and shows by calculation that, even if any were formed at this temperature, it would be highly improbable that we could cool it quickly enough to prevent its complete decomposition. The electrolytic preparation of ozone, especially the influence of the composition of the electrolyte and the character of the electrodes, has been discussed at length by Gräftenburg (*Ztschr. anorg. Chem.*, **36**, 355-379) and Kremann (*Ibid.*, **36**, 403-411.) Schenk and Richarz (*Sitzungsbr. Preuss. Akad.*, 1904, pp. 37-45 and 490-493; *Phys. chem. Centrbl.*, **1**, 690 and 707) point out the similarity between ozone and the emanations from radioactive bodies and advance a theory of ozone formation through the agency of gas ions. Part of the luminescence of zinc blend under the influence of radium radiation is attributed to ozone, which, the authors show, has the power of making zinc blend luminous, at the same time oxidizing it to the sulphate. In an atmosphere of carbon dioxide, the screen did not fluoresce so strongly under the radium rays. Schenk and Mihr (*Ber. chem. Ges.*, **37**, 3464-3467) have continued this work.

Appended is a list of publications of physico-chemical interest which have appeared during the period covered by the above review.

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VAN'T HOFF, J. H. (transl. A. SMITH).—Physical Chemistry in the Service of the Sciences. Decenial Publications of University of Chicago. Series 2, volume XVIII. 123 pp. The University of Chicago Press, 1903. $1.50.

MENDELÉEFF, D. (trans. G. KAMENSKY).—An Attempt toward a Chemical Conception of Ether. 51 pp. Longmans, Green & Co., London, 1904. 2s. net

MOISSAN, H. (transl. V. LENHER).—The Electric Furnace. The Chemical Publishing Co., Easton, Pa., 1904. $2.50. A second translation by A. F. de Mouilpied has been published by Longmans, Green & Co.

NERNST, W. (transl. C. S. PALMER and R. A. LEHFELDT).—Theoretical Chemistry. Second English from fourth German edition. 771 pp. Macmillan & Co. $3.75.

RECENTLY ESTABLISHED JOURNALS.

Electrochemical and Metallurgical Industry (first two volumes "Electro Chemical Industry").—Edited by E. F. Roeber, began Jan., 1903; 12 numbers a year (1 vol.). The Electrochemical Publishing Co., N. Y. $2.00 per year.

Journal de Chimie Physique.—Edited by P. A. Guye, began 1903; 8 to 10 numbers form yearly volume of 600 to 700 pp. Gauthier Villars, Paris. 25 Francs per volume.

Physikalisch chemisches Centralblatt. Edited by Max Rudolphi in Darmstadt. Began with year 1904. 24 numbers form yearly volume. Vol. I, 808 pp. Reviews are printed in German, English or French. Gebr. Borntraeger, Leipzig. 30 Marks per year.

Zeitschrift für wissenschaftlicher Photographie, Photophysik und Photochemie.—Edited by H. Kayser, E. English and K. Schaum. Began March, 1903. 12 numbers a year (1 vol.). J. A. Barth, Leipzig. 20 Marks per year.

NEW BOOKS.

ELECTRIC FURNACES AND THEIR INDUSTRIAL APPLICATIONS. BY J. WRIGHT. New York: The Norman W. Henley Publishing Co., 132 Nassau Street. Price, $3.00.

In fourteen sections, as they are called, covering 283 pages, the author presents most interesting and very instructive data in regard to electric furnaces. In the first three sections the various kinds of furnaces are presented, accompanied by historical and general statements of value. Thus mention is made that "the

natural gases, petroleum, bitumen, graphite, corundum, etc., ...can be artificially produced.....by the direct or indirect aid of the electric furnace." Considerable detail is given to the discussion of the production of carborundum. Acheson first made this substance in 1893, manufacturing in that year 6¾ tons of it, and in 1902 nearly 3,000 tons.

Taylor's carbon bisulphide furnace is the only furnace mentioned in connection with that industry. By means of it considerably more than 5,000 pounds of carbon bisulphide can be made in twenty-four hours.

The production of calcium carbide is exhaustively treated in about 48 pages. Almost every form of furnace, applied in this work, is discussed. "The cost of calcium carbide manufacture must necessarily be governed by local conditions, source of power, cost of raw materials, etc., so that it is impossible to formulate any hard and fast rule on the subject."

The presentation "of iron and steel in the electric furnace" will fix the reader's attention and prove highly suggestive. The production of other metals in the electric way is also considered.

The chapter devoted to phosphorus is necessarily brief. The main difficulty experienced in its manufacture in the electric furnace "is the necessarily high temperature at which the vapor leaves the furnace chamber. "Tatlock is authority for the statement that one-half the world's production of phosphorus, about 1,000 tons, was manufactured in the electric furnace (1899). The limited space allowed this review precludes a description of any one of the furnaces used for this particular purpose. If they actually yield the quantities indicated, it surely cannot be long before electrolytic phosphorus will be the only phosphorus handled in trade.

The glass manufacture in the electric way is touched upon. It is very evident that much experimentation will be required in this direction before speaking enthusiastically, although the preliminary trials have been encouraging.

The well known processes used in making aluminium receive fair consideration. In 1903 there were "nine factories engaged in the production of aluminium, either by the Hall or Heroult process; they are located as follows: America, 3; United Kingdom, 1; France, 2; Germany, 1; Switzerland, 1; Austria, 1. The several plants operated and controlled by the Pittsburg Reduction Co.

are capable of manufacturing 4,500 tons of aluminium per annum.

Various other metals claim moderate consideration. Thus, of calcium it is said to be "of great value in various industries as a reducing agent, the only drawback to its wide-spread use being its comparatively high market value." The schemes developed by Borchers and by Arndt for making electrolytic calcium are the only processes described. The plan of Rathenan and that of Goodwin appeared after the author had passed his manuscript to the publisher, so in that way their absence is explained. By these latter methods, so much alike, yet developed independently of one another, it would seem that the problem of calcium manufacture has really been solved. The applications of the metal now await development. It will be of interest to learn how well strontium and barium can be isolated electrolytically.

The concluding sections consider the application of the electric furnace to scientific research, tube furnaces, electrodes, efficiency and theoretical considerations, measurement of furnace temperatures, etc.

The book is an excellent compilation. It will be read with great interest by all chemists and will surely suggest new ideas and possibilities to the student of theoretical and practical electrochemistry. Its appearance is very timely.

EDGAR F. SMITH.

THE SESQUITERPENES. A monograph. By OSWALD SCHREINER, with a preface by EDWARD KREMERS. 130 pp. Pharmaceutical Review Pub. Co., Milwaukee, Wis., 1904. Price, $1.00.

This is Monograph No. 9 in the Pharmaceutical Science Series, edited by Dr. Kremers. Numerous investigations have been conducted in the field of terpene chemistry during the past twenty years, and yet but little knowledge has been accumulated concerning the chemical character of the so-called "sesquiterpenes," $C_{15}H_{24}$. The author has collected, classified and arranged, in convenient and readily accessible form, the scattered facts on record about this interesting group of compounds, and the resulting monograph constitutes a concise resumé of our knowledge of the subject. The arrangement of the matter is as follows: I, Introduction. II, General Part—(1) The position of the sesquiterpenes in the various systems of classification of terpenes at large $(C_5H_8)_x$; (2) The position of the sesquiterpenes in the modern rational system of classification of hydrocarbons; (3) classification and com-

parison of the better known sesquiterpenes and discussion of possible constitution and synthesis; (4) the occurrence of sesquiterpenes in the vegetable kingdom. III, Special Part.—The classification based upon the "modern rational system" referred to above (II, 2) takes cognizance of the fact that the $C_{15}H_{24}$ hydrocarbons belong to the C_nH_{2n-6} class, and may, therefore, exist in the following structural forms: (1) Straight chain compounds with four unsaturations; (2) Monocyclic compounds with three unsaturations; (3) Dicyclic compounds with two unsaturations; (4) Tricyclic compounds with one unsaturation; (5) saturated tetracyclic compounds. It is then shown (II, 3) how the various sesquiterpenes may be marshaled under these five headings. The Special Part (100 pages) takes up the individual sesquiterpenes alphabetically and discusses them in detail. Full references to the literature are given and a good Index concludes the work.

The author has done a real service to organic chemists in the compilation of this monograph, and it should prove of special value to all interested in the chemistry of the essential oils.

M. T. BOGERT.

CHEMICAL STATICS AND DYNAMICS. By J. W. MELLOR. Longmans, Green & Co. 1904. viii + 528 pp. Price, $2.00.

The book opens with a historical sketch, "from the beginning" to the year 1771, followed by illustrations of the meaning of "velocity "and an explanation of the use of mathematics in chemistry; the Introduction closes with 9 pages of energetics of the usual vague type.

The next four chapters are devoted to the rate of chemical change in homogeneous systems, including parallel, opposing and consecutive reactions; Chapter VI is "on the beginning of a chemical reaction," Chapter VII on "heterogeneous" reactions, and Chapter VIII on chemical equilibrium. The remainder of the book, rather more than half, contains chapters on Electrolytic dissociation, Catalysis and theory of chemical change, Fermentation, the Influence of temperature and pressure on rates and equilibrium, and Explosions.

The calculus is employed throughout, the best settings of various differential equations are discussed, and numerical examples are worked out in illustration ; but though evidently of the opinion that "ere long mathematics will be as useful to chemists as the

balance" the author emphasizes "the danger of bowing down and worshipping the mathematical fetish," and insists that a clear physical conception must precede the application of mathematics. A table of $\log_{10} \frac{1}{(1-x)}$ to four places is given as appendix.

More than 3,000 references are made to the literature, and in many cases the claims of English chemists are vindicated to honors hitherto held by foreigners. Schönbein's theory of autoxidation is "the Brodie-Schönbein theory"; Turner first discovered negative catalysis, and one of Ostwald's favorite illustrations is introduced as "Lieving's Switchback." American authors have not come off so well. van't Hoff and Planck get credit for formulas due to Gibbs; the "law of successive reactions" is Ostwald's law, while the useful distinction between "bimolecular" reactions and "reactions of the second degree," introduced by Noyes, is ignored.

More important is the question of nomenclature, on which the books of this series may exert a decisive influence. In the interest of clearness it is hoped that in the next edition "side reactions" may be replaced by "parallel" or "subsidiary" reactions, as the case may be; that "catalyst"—unpleasantly reminiscent of "typist" and "scientist"—may be dropped; and that "concentration" may be kept to its own meaning, and not be confounded with the wholly different conceptions of quantity and active mass.

In spite of these minor defects the book may be heartily recommended to all interested in chemical mechanics; for, although in many instances the standpoint of the author may not meet with general acceptance, all his readers will agree that the little volume is a real addition to chemical literature, and is in no sense a rehash of the standard German works. W. LASH MILLER.

CORRECTIONS.

In the March number of the Journal, page 312, line 27, should read: "N. D_{100} = density in amperes for *100* square centimeters."

In the article on "Radioactivity as an Atomic Property" in the April number, page 394, the parenthesis should be omitted from the equation given.